# A COMPARATIVE STUDY OF THE BCR SEQUENTIAL AND BATCH EXTRACTIONS FOR WASTES AND WASTE-AMENDED SOIL

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# ABSTRACT

The use of standard soil tests to assess waste materials has become a common practice in waste management. However, the suitability of using standard soil tests on waste materials is questionable. Therefore, this investigation was undertaken to compare commonly used chemical extraction methods for their ability to extract elements from soil, waste, and soil-waste mixtures. This was carried out by:

- Assessing the effects of extraction time on the extractability of Al,Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb, S, Si, and Zn;
- Assessing the comparability between single and sequential extraction.

Two manganese rich wastes namely electro-winning waste (EW) and silicate-rich smelter slag (SS) and an acid soil (Inanda, Ia) were used for this study. Waste amended soils were obtained by incubating the EW and SS with Ia soil at field capacity at a rate of 20 g $kg^{-1}$ and 120 g $kg^{-1}$ soil respectively, and were sampled at day 0, 7, 28, 56, and 140.

The effect of extraction time was assessed on the EW, SS, and Ia soil with carbonated water used in the acid rain test conducted at 16, 20, 30, and 50 hours. The equilibration time was different for different materials and elements. The concentration of Al and Zn did not change appreciably with increasing extraction time in the EW. Similar results were found for Mg, S, and Si in the SS and S in the Ia soil. This was attributed to ‘equilibrium’ being reached before 16 hours. The equilibration time of 20 hours which would release the exchangeable and specifically adsorbed elements was obtained for Co, Mg, Si, S, and Mn in the EW. The concentration of Ca decreased with extraction time in the EW and was attributed to readsorption. The concentration of Ca and Mn in the SS and Al, Fe, and Si in the Ia soil increased with extraction time and the ‘equilibrium’ was not reached even after 50 hours. This was attributed to the release of elements due to dissolution of minerals.

In the comparison between Community Bureau of Reference (BCR) sequential and batch extraction, the concentrations of Ca, Co, Mg, Mn, and S were higher in batch

extraction than in sequential extraction, particularly for the EW and the EW treated soils. This was possibly caused by the readsorption of released elements during water extraction. On the contrary, sequential extraction had higher concentration of Al and Fe compared to batch extraction for the EW, Ia soil, SS treated soils, and EW treated soils. These were attributed to a continued desorption of elements and dissolution of minerals due to exposed surfaces which occurs in sequential extraction.

The comparison between single and sequential extraction for the BCR sequential extraction showed that hydroxylammonium chloride (HAC) applied in sequential extraction had higher concentration of Al, Co, Fe, Pb, and Zn than the single HAC extraction. This was probably due to incomplete dissolution of minerals, precipitation of amorphous minerals, and readsorption of released elements occurring for a single HAC extraction. These were minimised for hydrogen peroxide ($H_2O_2$) extraction and hence comparability between single and sequential $H_2O_2$ extraction was observed. This was probably due to the presence of complexing agent in the extracting reagent which would minimise the formation of secondary precipitates and hence, improved dissolution of minerals was obtained. Similarly, the concentrations of elements were comparable between single and sequential aqua regia extraction. These results indicated that comparability is improved between single and sequential extraction when aggressive conditions are used.

The results from this investigation indicated that when chemical extraction methods are applied to wastes, the effects of the waste properties on the results of extraction need to be well understood. Consequently, when the chemical extraction methods are used in waste management scenarios certain modifications might have to be made. These modifications include the use of a high solution:solid ratio and an extracting solution which has high complexing ability.

# PREFACE

The work described in this thesis was carried out in the School of Environmental Sciences, University of Kwa-Zulu Natal, Pietermaritzburg, from January 2008 to October 2010, under the supervision of Mr H.C. Bester and Dr. L.W. Titshall.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

Elements in the soil and waste exist in various chemical 'pools', which can be divided into three main categories i.e. those in solution (readily available), labile (available) and non-labile (non-available) elements. Readily available elements exist as free ions, ions complexed by soluble organic matter, and soluble salts (Miller *et al.*, 1986; Van Herck and Vandecasteele, 2001; Filgueiras *et al.*, 2002). Available elements are often found on the exchange sites, precipitated as pure or mixed solids, and adsorbed on inorganic and organic constituents (McLean and Bledsoe, 1992). Non-available elements are associated with insoluble primary and secondary minerals. It is important to separate and identify the various chemical 'pools' for assessment of agricultural and ecological toxicity problems.

Soil testing (as defined by Melsted, 1967) is "*any chemical or physical measurement made on a soil*". It is an invaluable tool used for the separation and identification of chemical 'pools'. During soil testing, different chemical extraction methods are used to quantify elements in terms of their association with the different 'pools' or solid phases. The single and sequential extraction methods were developed in an attempt to partition elements into readily available, available, and non-available fractions. The purpose of these extractions is to quantify elements from different 'pools' in a soil so that the variation in the amount extracted reflects the variation in the amount that will either be taken up by plants or migrate to groundwater. Hence these methods have been used for making fertiliser recommendations, as a guide in estimating the mobile phase in solute movement problems, and in the assessment of toxicity problems (Ure, 1995).

Soil toxicity problems may be due to pollution of soils by elements from natural and anthropogenic inputs. These have been assessed by determining the total concentration of an element in soil. The total elemental content is often determined by using strong acids (e.g. $HNO_3$, HCl, HF, $HClO_4$, and $H_2SO_4$) or a combination of these acids. The

purpose of the strong acid is to dissolve the solid phases in soils using aggressive (heating) digestion techniques (McLean and Bledsoe, 1992; McLaughlin *et al.*, 2000). The measurement of total elemental content using the 'strong acids' technique quantifies the sum of readily available, available, and non-available. However, it does not distinguish the association of an element with different 'pools' in the soil, nor does it indicate the amount of an element that may be potentially available or mobile. Thus, it has been recognised that this measurement provides little indication of an element's potential toxicity, its potential interaction with biotic and abiotic components present in soils, and its impact on the environment (Tessier and Campbell, 1988; Mester *et al.*, 1998).

Adequate assessment of pollution and the degree of contamination requires that the readily available, available, and non-available fractions are measured separately. Generally, unbuffered salts, weak dilute acids, complexing agents, reducing and oxidising agents are used when attempting to quantify elements with each of these fractions. These reagents extract elements from different compartment in soils.

Unbuffered salts are often used to determine easily soluble and exchangeable elements. Such elements have been correlated to migration to groundwater and plant uptake (McLean and Bledsoe, 1992; Gupta *et al.*, 1996). Complexing agents have been reported to extract elements associated with Fe-Mn oxides, carbonates, and organic matter. Results from complexing agents extraction are closely correlated to plant uptake (Bermond and Ghestem, 2000; Kashem and Singh, 2001; Hlavay *et al.*, 2004). Elements associated with stable organic matter and Fe-Mn oxides, in particular, are mobilised by changes in redox status of the soil and are often determined using oxidising and reducing agents, respectively (Almas and Singh, 2001).

Elements in waste materials, like in soils, exist in various compartments which may explain why soil tests have been used in the assessment of contaminated soils and also in waste management. These soil tests provide useful information regarding waste properties. However, results obtained often have different environmental implications

compared to results obtained from the analysis of soils. Some aspects that need to be considered when interpreting results from waste are:

- differences in extraction times and soil solution ratios required to ensure equilibrium is reached and to account for differences in elemental concentration between 'normal' soils and wastes or waste contaminated soils;
- effects of dilution and interaction of waste with soil; and
- can the waste material be disposed off at landfill, dedicated 'monofill', or onto agricultural (as a soil ameliorant) land?

Different chemical extraction methods have been developed to assess possible adverse effects associated with each of the management (waste disposal) strategies. The existence of different extraction methods used for differentiating waste materials and waste management practices, in addition to soil tests, has resulted in the multiplication of the methods that assess the likelihood of toxicity (Quevauviller *et al.*, 1996a; Sahuquillo *et al.*, 2003). Furthermore, most of these chemical extraction methods have been used outside the context for which they were developed. Quevauviller *et al.* (1996a) justified this practice by indicating that an overlap exists between soils, contaminated soils, and waste. This overlap is based on the fact that contaminated soils (soil/ waste mixtures) inherit some of their properties from wastes and some from the soil (Cameron *et al.*, 1997). Quevauviller *et al.* (1996a) indicated the need to identify differences and similarities in the chemical extraction methods used for waste and soils.

## 1.2 Background

In a study investigating the potential to dispose of two different Mn-rich waste to land, Titshall (2007) used various standard methods to characterise waste materials and soils, and also infer environmental risks associated with these wastes. However, the applicability and relevance of using soil assessment tests for waste management practices was questioned, and transferring guidelines from one system to another could be problematic (O'Connor, 1988; Cameron *et al.*, 1997; Kasselman, 2004). Some of the concerns regarding the use of standard methods to characterise wastes were:

- Are soil tests valid for a waste materials and waste treated soils?

- Are the results from common tests and risk assessment procedures comparable?
- Do results from the test methods have any practical value from a characterisation and risk assessment perspective?

The above questions form the basis for this study.

## 1.3 Aims and objectives

The overall aim of this study was to investigate the use of various extraction procedures in both pure waste and waste contaminated soil. The investigation included a comparison of commonly used chemical extraction methods in their abilities extract elements from soil, waste, and soil/waste mixtures. The specific objectives were:

- to investigate the extractability of elements as a function of extraction time (i.e. time the extracting reagent is in contact with the material),
- to investigate the changes in the availability of elements in waste amended acid soil as a function of incubation time (i.e. contact time of waste with soil),
- to determine whether it is necessary to include the water soluble and exchangeable fractions in the Community Bureau of Reference (BCR) sequential extraction procedure (Quevauviller *et al.*, 1994), and
- to compare the results obtained from the BCR sequential extraction to single extraction procedure using the same reagents and extraction conditions.

## 1.4 Outline of Thesis

The chapters presented in this document attempt to address questions mentioned above. This was achieved by three main activities, namely, literature review, collection of pre-existing data, and a series of laboratory experiments. The outline of chapters is presented below.

- **Chapter 2**: A literature review covering reagents used to estimate the concentrations of elements that are phytoavailable or mobile. The tests reviewed are used in soil testing and some in waste management. The literature will also discuss the differences and similarities between these reagents.

- **Chapter 3**: Two waste materials and one soil were used. Existing data on basic physiochemical properties of these materials is discussed with implication for land disposal and chemical extraction methods.
- **Chapter 4**: Investigates the variation in the extractability of elements as a function of extraction time using carbonic acid.
- **Chapter 5**: Assesses the distribution of elements in wastes and soil using the BCR sequential extraction procedure.
- **Chapter 6**: Investigates the changes in the availability of elements from a waste amended acid soil as a function of incubation time.
- **Chapter 7**: Compares the results obtained by applying distilled water, ammonium nitrate, and acetic acid extraction as sequential (successive) extraction to those obtained by applying these reagents as single batch extractions.
- **Chapter 8**: Compares the results obtained by applying the BCR sequential extraction reagents as sequential (successive) extraction to those obtained by applying the same reagents as single batch extractions.
- **Chapter 9**: Concludes by discussing the overall implications of the results and attempts to answer the main questions posed.

# CHAPTER 2

# A REVIEW OF DIFFERENT REAGENTS USED TO ASSESS METAL RELEASE FROM SOILS AND INDUSTRIAL WASTES

## 2.1 Introduction

Chemical extraction methods were developed to simulate natural processes that result in the release of an element from solid phases into soil solution (McLean and Bledsoe, 1992; Ross, 1994; Quevauviller *et al.*, 1996a; Singh, 2006). Elements in soil solution can either be taken up by plants or migrate to groundwater (Figure 2.1). They can also get readsorbed on solid phases or form new minerals (Figure 2.1). Thus chemical extraction methods have been used to predict the likelihood of agricultural and ecological toxicity of elements under different environmental conditions. Results from chemical extractions are therefore used to guide waste management strategies (US-EPA, 2003; Townsend *et al.*, 2003a).

A number of chemical reagents have been used to quantify the release of elements into soil solution. Most of these reagents attempts to imitate one or more of the equilibria presented in Figure 2.1. Tests such as diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA), toxicity characteristic leaching procedure (TCLP), the acid rain test (ART), and various sequential extraction procedures (SEP) are frequently used to quantify the concentration of pollutants that will be released from soils and waste into soil solution (Lindsay and Norvell, 1978; Cabral and Lefebvre, 1998; Li *et al.*, 2001; Voegelin *et al.*, 2003; van Elteren and Budic, 2004; Silveria *et al.*, 2006; Sànchez-Martín *et al.*, 2007).

The DTPA and EDTA extractions are intended to estimate the concentration of elements that are potentially available for plant uptake. The TCLP and ART are used to estimate the amount of elements that can migrate to groundwater. The SEP are intended to estimate the quantity of elements retained in the different solid-phases such as carbonates, oxides, organic matter and silicates. In SEP, a number different reagents are used, each intended to extract a defined portion or phase of an element.

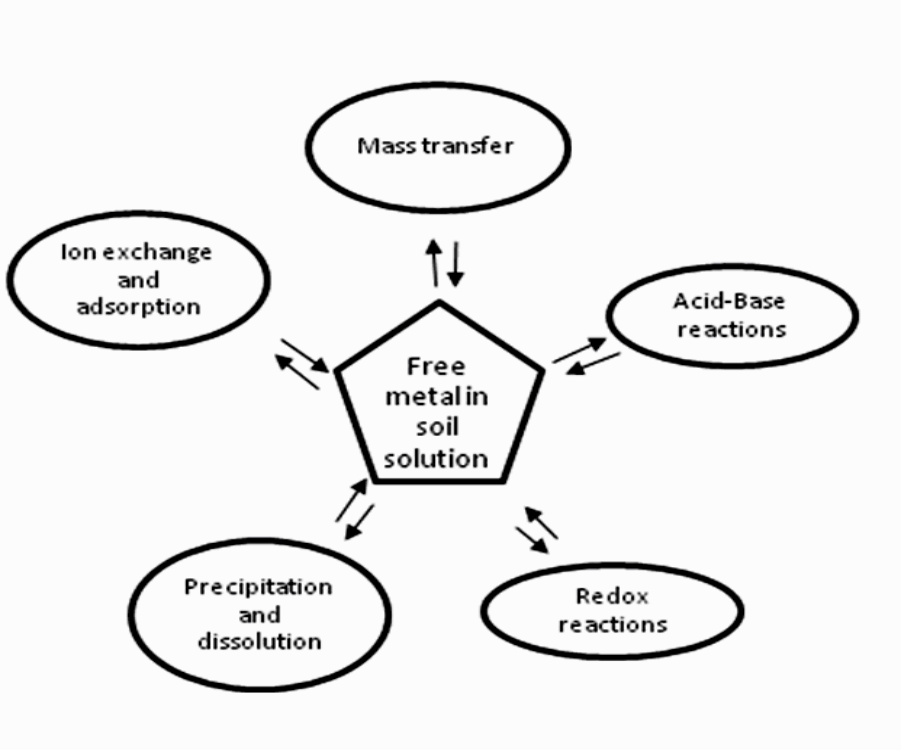



**Figure 2.1** Factors controlling the release and removal of pollutants in soil solution (McLean and Bledsoe, 1992).

This review discusses the reagents that are used to estimate the concentrations of elements that are phytoavailable or mobile. It will also discuss the differences and similarities between reagents used in different extraction methods. In addition, the development of sequential extraction procedures (SEP) and a detailed overview of reagents used in the BCR SEP (Quevauviller *et al.*, 1994) will be discussed.

## 2.2 Extraction of phytoavailable elements

The movement of nutrients and heavy metals to, and uptake by plants, occur through passive and active transport mechanisms. Uptake by the root can take place through mass transfer (Figure 2.1). Roots can exude protons and chelating agents that release elements bound to soil solid phases thus increasing their availability for plant uptake (McBride 1994).Therefore, these mechanisms need to be considered when estimating the concentrations of nutrients and contaminants in the soil that may be available for plant uptake. Extractants commonly used for this purpose include acid solutions, neutral

salts and chelating agents (Krishnamurti *et al.*, 1995; Chen *et al.*, 1996; Gupta *et al.*, 1996; Kennedy *et al.*, 1997).

### 2.2.1 Chelating Agents

Enhanced uptake of nutrients by plants caused by the addition of chelating agents is well established (Lindsay and Norvell, 1969; Evangelou *et al.*, 2007). Chelating agents enhance nutrient uptake by forming soluble complexes with nutrient and retaining them in solution. The soluble complexes prevent readsorption of nutrients and precipitation of secondary amorphous minerals. Since chelating agents increase availability of nutrients in soils, they have been used to quantify nutrients available for plant uptake (Viro, 1955; Lindsay and Norvell, 1978; McLaughlin *et al.*, 2000; Evangelou *et al.*, 2007).

There are two proposed mechanisms through which chelating agents increase availability of elements. Both mechanisms involve ion exchange with a metal chelate ion pair. The first possibility is that the chelating agent form complexes with free ions in solution resulting in reduced ion activity. As ion activity is reduced, elements are desorbed from the soil surface to replace the complexed ions removed from solution, in accordance with the Le Chatelier's Principle (Cajuste and Laird, 2000; Singh, 2006). The second possibility is that the nutrient (N) on soil surface is paired with a ligand (L) which is supplied by a metal ligand salt (ML) (Equation 2.1). The nutrient is then desorbed from soil surface and retained in solution in a complexed form (NL) for analysis of heavy metals and nutrient content (McLaughlin *et al.*, 2000).

$$\text{Soil—N} + \text{ML} \rightarrow \text{Soil—M} + \text{NL} \qquad \textbf{2.1}$$

The DTPA and EDTA are two of the most commonly used chelating agents. The DTPA method was developed to estimate phytoavailable micronutrients in near neutral and calcareous soils (Lindsay and Norvell, 1978). In contrast, EDTA is considered to extract elements available for plant uptake in non-calcareous acid soils (Viro, 1955; Kennedy *et al.*, 1997; Sahuquillo *et al.*, 2003).

The DTPA extraction was originally developed to assess the need of fertilisation in nutrient deficient soils. It uses 20 ml of DTPA reagent to extract 10 g of soil for 2 hours. The DTPA reagent is buffered at pH 7.30 and consists of 0.005 M DTPA, 0.1 M triethanolamine (TEA) and 0.01 M calcium chloride ($CaCl_2$). The DTPA complexes the free metal ions in solution and results in desorption of metals from soil surfaces while TEA acts as a pH buffer. Calcium chloride suppresses dissolution of calcium carbonate ($CaCO_3$) and balances the $CaCO_3$ equilibrium at $CO_2$ levels about 10 times that of the atmosphere (Lindsay and Norvell, 1978; O'Connor, 1988). The addition of $Ca^{2+}$ from $CaCl_2$ favours the formation of $CaCO_3$ (Equation 2.2) which minimises the release of $CO_2$ (Equation 2.3).

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad \textbf{2.2}$$

$$CO_3^{2-} + H_2O \rightleftharpoons CO_2 + 2OH^- \qquad \textbf{2.3}$$

On the other hand, EDTA extraction uses 20 ml of EDTA reagent to extract 2.00 g of soil for 1 hour. The EDTA reagent is made up of 0.05 M EDTA which is adjusted to pH 7 by addition of ammonium hydroxide. The ammonium ion in this reagent replaces nutrients on soil surfaces which is then complexed by EDTA and retained in solution (Viro, 1955; Bermond and Gershem, 2001).

When DTPA and EDTA were compared, EDTA was found to extract higher amounts of micronutrients than DTPA (Norvell, 1984; Chen *et al.*, 1996; Quevauviller *et al.*, 1996b; Sahuquillo *et al.*, 2003; Walker *et al.*, 2003; Gupta and Sinha, 2006; Hseu, 2006). Sahuquillo *et al.* (2003) reported that the concentration of Cd, Cr, Cu, Ni, Pb, and Zn extracted by EDTA were between 1.5 and 5 times higher than those extracted by DTPA. There are two possible aspects that might explain why EDTA is extracting higher concentration of elements compared to DTPA. The first one is that the liquid/soil ratio (l/s) and concentration of EDTA (10 (l/s) and 0.05 M) is higher than that of DTPA (2 (l/s) and 0.005 M). The low concentration and liquid/ soil ratio of DTPA reagent used can results in saturation of the extracting solution in soil of high metal loadings. Whereas, EDTA is less prone to saturation and that is why EDTA is used to extract elements in contaminated soil (McLaughlin *et al.*, 2000).

The second aspect is that EDTA reagent is not buffered with respect to pH and can results in decreasing pH during extraction. The decreasing pH can cause dissolution of carbonates which is minimised in the DTPA extraction (Viro, 1955; Lindsay and Norvell, 1978). In addition, the decreasing pH can also cause EDTA to overestimate the concentration of elements that are available for plant uptake. In an attempt to highlight the aggressive nature of EDTA, McGrath and Cegarra (1992) suggested that the concentration of an element extracted with EDTA was equivalent to thousand years of uptake by a plant.

Both EDTA and DTPA extractions are often used to estimate concentrations of elements under conditions that differ from those for which they were developed. Under such circumstances, users are advised to be aware of possible consequences which may result in unreliable prediction of plant available of nutrients (O'Connor, 1988). Saturation of extracting solution and changing pH during extraction contribute to unreliable prediction of plant available nutrients. Thus, the use of DTPA in acid soils, in metals (other than Zn, Mn, Cu, and Fe), and in assessing the toxic effects of adding waste to soils should be done with caution (O'Connor, 1988).

2.2.2 Neutral salts

Plant roots exude cations (especially $H^+$) which cause cationic nutrients to be desorbed from soil surfaces (Kabata-Pendias, 2001). This mechanism is referred to as cation exchange where cations adsorbed on soil surfaces can be exchanged by another cation which has a higher replacing power depending on valency and ion concentration (Tan, 1998; McLaughlin *et al.*, 2000). Cations which include $Ca^{2+}$, $Ba^{2+}$, $NH^{4+}$, and $H^+$ are known to have a high replacing power (Tan, 1998). Hence, the concept of cation exchange is the basic principle underlying the use of neutral salts to estimate plant available elements (particularly metal cations). The cation of the extracting salt solution replaces the cations on soil surfaces (McLaughlin *et al.*, 2000). This brings the exchanged cation into solution and available for analysis.

The most frequently used salts to estimate the concentrations of plant available elements are ammonium nitrate ($NH_4NO_3$, 1.0 M), ammonium acetate ($NH_4OAc$, 1.0 M), and $CaCl_2$ (0.01 M) (Haq *et al.*, 1980; Gupta *et al.*, 1996; Sterckeman *et al.*, 1996; Kabata-Pendias, 2001; Menzies *et al.*, 2007; Khan *et al.*, 2009). There is a disagreement in the literature regarding the salt extractant that best correlates to plant available elements. Most studies seem to agree that $NH_4OAc$ is a stronger extractant than $NH_4NO_3$ or $CaCl_2$ (Gupta and Sinha, 2007; Meers *et al.*, 2007a; Wang *et al.*, 2009). This could be arising from the fact that $NH_4^+$ cation has high replacing power and that acetate anion can complex and retain released elements in solution.

The solution of 0.01 M $CaCl_2$ represents the ionic strength of many soils and extracts low concentration of elements compared to other salts (Kabata-Pendias, 2001; Sahuquillo *et al.*, 2003; Meers *et al.*, 2007b). As such, $CaCl_2$, is suggested to be a good indicator of risk and many authors still regard $CaCl_2$ as a preferred extractant for estimating plant available elements (Sahuquillo *et al.*, 2003; Pueyo *et al.*, 2004; Meers *et al.*, 2007b).

Extraction with 1 M $NH_4NO_3$ (1:2.5, solid:solution ratio) was proposed by the Deutsches Institut fûr Normung (DIN) to assess mobility and availability of contaminants in the soil (DIN, 1997). The South African Department of Water Affairs and Forestry (DWAF, now known as Department of Water and Environmental Affairs) has adopted the use of this reagent for assessing the risk of applying sewage sludge on agricultural soils (DWAF, 2005a). McLaughlin *et al.* (2000) has also indicated that 1 M $NH_4NO_3$ is the best indicator of plant available Cd and Zn in contaminated soils.

Different extraction methods ($NH_4NO_3$, $NH_4OAc$-EDTA, and $HNO_3$) were compared in a study conducted by Forsberg and Ledin (2006) investigating the effect of sewage sludge on the availability of Al, Mn, Cu, Zn, Ni, Pb, As, Cr, and Cd in oxidised mine tailing. These authors reported that the concentration of these elements in the $NH_4NO_3$ extracts for sewage sludge, treated and untreated tailings were positively correlated with the uptake of elements by barley grain and red fescue. However, on oxidised tailings (collected at the time of harvesting), $NH_4OAc$-EDTA was a better indicator of plant

uptake compared to $NH_4NO_3$. One of the findings of their study was that milder extractants' prediction of plant uptake of heavy metals was better than that of aggressive extractants.

## 2.3 Leachability tests

The aim of leaching tests is to assess the likelihood of groundwater contamination. Some commonly used standard leaching procedures include the Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP), Extraction Procedure Toxicity (EP-TOX), and Acid Rain Test (ART) (Townsend *et al.*, 2003a; DWAF, 2005b). Another regularly used extractant is distilled water (DW). Typically, these tests are conducted by batch extraction procedures. Sometimes these tests are adapted by using leaching columns (that mimic soil or waste vertical profiles) and analysing leachates collected from the columns. These are referred to as column leaching tests (CL). This section of the review will focus on TCLP, ART, DW and CL, as these represent the most commonly used methods in the assessment of waste and soil leaching potential.

### 2.3.1 The TCLP and ART extractions

The TCLP and ART are intended to simulate leaching of pollutants from wastes at a landfill site and a dedicated 'monofil' site, respectively (DWAF, 2005b). The TCLP is intended to mimic leaching of pollutants by organic acids generated in a landfill site (Kasselman, 2004; DWAF, 2005b). Two extracting solutions are used in TCLP extraction, depending on the pH of the waste material. For waste with an alkaline pH an acidic solution of dilute acetic acid (pH 2.88 ± 0.05) is used, while an acetic acid solution with the pH adjusted to 4.93 ± 0.05 using 1 M sodium hydroxide is used for acid waste materials (DWAF, 2005b).

The ART is intended to estimate leaching of pollutants in mineral waste that has been monofilled and exposed to 'clean' rainfall. It is based on the premise that carbon dioxide is dissolved in rainwater to produce carbonic acid that can potentially leach both inorganic and organic pollutants (DWAF, 2005b). As a result, saturated carbonic acid solution (pH 3.6 – 3.8) is used as an extracting solution.

The concentrations of pollutants extracted by TCLP and ART are compared to the limits set out in 'The minimum requirement for the handling, classification and disposal of hazardous waste' (DWAF, 2005b; Titshall, 2007). These limits are referred to as the 'acceptable environmental exposure' (AEE) and the 'acceptable human health exposure' (AHHE; DWAF, 2005b). The AEE and AHHE indicate the concentration of a pollutant that will have minimal impact on the environment and human health, respectively (DWAF, 2005b). The AEE and AHHE values are the same for both TCLP and ART. However, the TCLP extraction often extracts higher concentrations of heavy metals compared to the ART (e.g. Titshall, 2007; Table 2.1). The differences between these two tests have been attributed to higher complexing ability, the strength, and the pH of TCLP extracting solution (Quevauviller *et al.*, 1996a; Chang *et al.*, 2001; Townsend *et al.*, 2003a; Sun *et al.*, 2006; Titshall, 2007).

While the TCLP and ART were originally developed for landfilling of wastes (DWAF, 2005b), both procedures have been routinely used to characterise wastes for use in land application, (Reynolds *et al.*, 2002; Titshall, 2007). Reliable prediction of pollutants leaching using TCLP under these conditions is questionable as conditions for land application are different to those of landfill. Several authors have also expressed concerns regarding the use of TCLP outside of the conditions for which it was originally intended (Murarka, 1999; Kasselman, 2004; Al-Abed *et al.*, 2006; George *et al.*, 2007).

The TCLP extraction has drawbacks which have been highlighted in literature. Firstly, TCLP extraction does not account for factors that control metal extractability such as pH, redox potential, particle size and contact time (Townsend et al., 2003b; Al-Abed et al., 2006). Secondly, TCLP extraction has been reported to underestimate the leaching of pollutants from a landfill (Ghosh et al., 2006). Lastly, Townsend et al. (2003b) and Ghosh et al. (2006) illustrated the limitations of TCLP in terms of representing the actual field conditions such as continuous leaching of pollutants over time and the presence of carbonates and phosphates. Nevertheless, TCLP is still used to classify waste materials. It is also acknowledged that there is no one single batch test (such as TCLP) that can best represent field conditions (Fernandez-Sempere et al., 1997).

**Table 2.1** A comparison between toxicity characteristic leaching procedure (TCLP) and acid rain test (ART) in extracting heavy metals from Pb/ Zn mine tailings (PT), manganese rich electro-winning waste (EW), and silicate rich smelter slag (SS) (Titshall, 2007)

| Material | pH ($H_2O$) | Test | Final extract pH | Cd | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | (mg $L^{-1}$) | | | | | | |
| **PT** | 8.20 | TCLP | 5.11 | bd | 1.00 | 5.45 | 59.9 | 0.06 | 12.5 | 93.6 |
| | | ART | 7.00 | 0.13 | bd | 0.04 | 1.18 | 0.03 | 0.19 | 26.9 |
| **EW** | 6.89 | TCLP | 5.09 | bd | 0.75 | 0.07 | 686 | 0.88 | 0.53 | 3.87 |
| | | ART | 7.32 | 0.05 | 0.02 | 0.10 | 217 | 0.45 | 0.39 | 0.37 |
| **SS** | 9.73 | TCLP | 7.81 | bd | bd | bd | 302 | 0.04 | 0.25 | bd |
| | | ART | 8.29 | 0.02 | 0.06 | 0.02 | 2.58 | 0.06 | 0.01 | bd |

*bd below detection

2.3.2 The distilled water extraction

Distilled (or deionised) water (DW) has also been used to assess the leaching potential of pollutants from waste. The DW extraction has also been used in soil testing (e.g. saturated paste). Leaching with DW represents mild conditions where relatively soluble and mobile pollutants can migrate to groundwater (Al-Abed *et al*., 2006). The assessment of risk with DW has been conducted in numerous studies and it has been proposed that this test determines short-term (immediate) release of pollutants (Chang *et al*., 2001; Kasselman, 2004; Al-Abed *et al*., 2006).

A number of studies have used both DW and TCLP extraction to characterise waste materials (Chang *et al*., 2001; Kasselman, 2004; Al-Abed *et al*., 2006). The main differences between DW extraction and other extractions that estimate the leaching of pollutants are extraction time, strength of the extracting solution and liquid-to-solid ratio. These factors are often the cause of differences in the concentration of pollutants extracted by different extraction methods.

When comparing TCLP to DW test, Chang *et al*. (2001) found that TCLP extracted more Cu, Pb, and Zn than distilled water (Table 2.2). In another study, DW extracted more Pb than TCLP in sewage sludge (Kasselman, 2004). However, no significant difference was observed for Cu and Zn extracted using from sewage sludge these tests (Kasselman, 2004).

**Table 2.2** A comparison between Toxicity Characteristic Leaching Procedure (TCLP) and Distilled Water (DW) in extracting Cu, Pb and Zn from different waste materials (Chang *et al.*, 2001)

| **Material** | **Test** | **Cu** | **Pb** | **Zn** |
|---|---|---|---|---|
| | | **(mg $L^{-1}$)** | | |
| **Electroplating sludge** | TCLP | 28 | <0.32 | 372 |
| | DW | 0.87 | <0.32 | 1.8 |
| **Dye-stuff sludge** | TCLP | <0.06 | <0.32 | 0.19 |
| | DW | <0.06 | <0.32 | <0.05 |
| **Incineration bottom ash** | TCLP | 0.44 | 27 | 0.14 |
| | DW | 0.58 | 6.2 | 0.96 |
| **Steel-mill bottom residue** | TCLP | <0.06 | <0.32 | 0.40 |
| | DW | <0.06 | <0.32 | 0.26 |
| **Leather debris** | TCLP | <0.06 | <0.32 | 0.10 |
| | DW | <0.06 | <0.32 | <0.05 |

In the leaching of mineral processing waste, DW extracted more Cu than TCLP, with no significant difference in the amount of Zn and Se extracted by these two extraction methods (Al-Abed *et al.*, 2006). However, the concentration of Pb extracted by TCLP was higher than that extracted using DW (Al-Abed *et al.*, 2006). Although different liquid-to-solid ratio and extraction time used for DW extraction could have played a role in differences observed between various studies, different materials used in leaching experiments might have had a major influence.

2.3.3 The column leaching tests

Distilled (deionised) water (DW) has also been used in column leaching tests (CL). The time a CL test is conducted can range from hours to over a year and predicts short, medium, and long-term release of pollutants from the waste (van der Sloot *et al.*, 1996; Jong and Parry, 2005; Rosende *et al.*, 2008). Column leaching tests are more representative of the field conditions as in these tests soils or wastes are packed in columns to mimic soil or waste vertical profiles (McLean and Bledsoe, 1992; Twardowska and Szczepanska, 2002; Townsend *et al.*, 2003b). After the soil or waste is packed, a leaching solution is applied to the material in a column followed by leachate collection and analysis. The advantage of this technique is that leaching solution can be applied at continuous flux, providing a fresh solution to extract and leach pollutants (Fallman and Aurell, 1996; Chang *et al.*, 2001; Townsend *et al.*, 2003b).

Rosende *et al*. (2008) indicated that CL tests yield accurate assessment of pollutant release. These authors pointed out that other extraction suffer from readsorption due to saturation of the extracting solution; the effect from adsorption phenomena is minimised in CL tests. However, CL tests have limitations. The main drawback of using CL tests is lack of reproducibility arising from clogging of pores or preferential flow (or channelling) through the column (McLean and Bledsoe, 1992; Townsend *et al.*, 2003b; van der Sloot *et al.*, 2003). Another limitation of CL test is the difficulty in controlling experimental conditions such as development of reducing conditions in the column (McLean and Bledsoe, 1992; Cao *et al*., 2003; Townsend *et al*., 2003b).

## 2.4 Sequential extractions

Single extractants do not account for the release of pollutant associated with changes in soil-solution chemistry (such as pH or redox potential) or different forms (or pools) of the pollutant. The potential migration and retention of pollutants in a soil system is strongly dependent on the chemical form of the pollutant and prevailing chemical conditions that may influence the speciation and ultimate mobility of the pollutant. The phase in which the pollutant exists in the waste or soil is often assessed using sequential extraction procedures (SEP). These are intended to extract the pollutant associated with certain phases and to simulate those reactions that can modify the concentration of

metals in soil solution, such as modifications of environmental conditions (Tessier *et al.*, 1979; Gleyzes *et al.*, 2002; Sahuquillo *et al.*, 2002).

Sequential extraction procedures aim to separate metals as exchangeable or bound in different solid phases such as carbonates, organic matter, silicates and Fe-Mn oxides (Tessier *et al.*, 1979). The exchangeable pollutants are considered as readily mobile (labile) while the silicate-bound elements are considered to be highly immobile and inactive (Kaasalainen and Yli-Halla, 2003, He *et al.*, 2005; Lu *et al.*, 2005). The carbonate-, Fe-Mn oxide-, and organic matter-bound pollutants are regarded as relatively active depending on the physical and chemical properties of the solid phase (Filgueiras *et al.*, 2002; He *et al.*, 2005; Lu *et al.*, 2005). In SEP, extractants are applied in order of increasing strength so that the successive fractions obtained correspond to metal forms of lesser mobility (Figure 2.2).

The main drawbacks of SEP have been long extraction times, lack of selectivity (attack of non-target phases) in reagents used, readsorption and redistribution of pollutants during the extraction, and incomplete dissolution of target phases. In addition, lack of uniformity in SEP such as different extraction times, use of different reagents and reaction conditions (Table 2.3) have been found to be problematic. The primary concern with lack of uniformity is that comparison of results obtained from different studies is very difficult.

In an attempt to standardise sequential extraction protocols, the Community Bureau of Reference (BCR, now known as SMTP: the Standards, Measurements and Testing Programme) proposed a three-step extraction procedure (Quevauviller *et al.*, 1994). This procedure could be used as a means of comparison of data of extractable metals in a solid sample (particularly soil and sediments). This protocol uses acetic acid extraction (Step 1), hydroxylammonium chloride extraction (Step 2), and hydrogen peroxide/ammonium acetate extraction (Step 3) which extract the acid-soluble, reducible and oxidisable fractions, respectively (Quevauviller *et al.*, 1994).

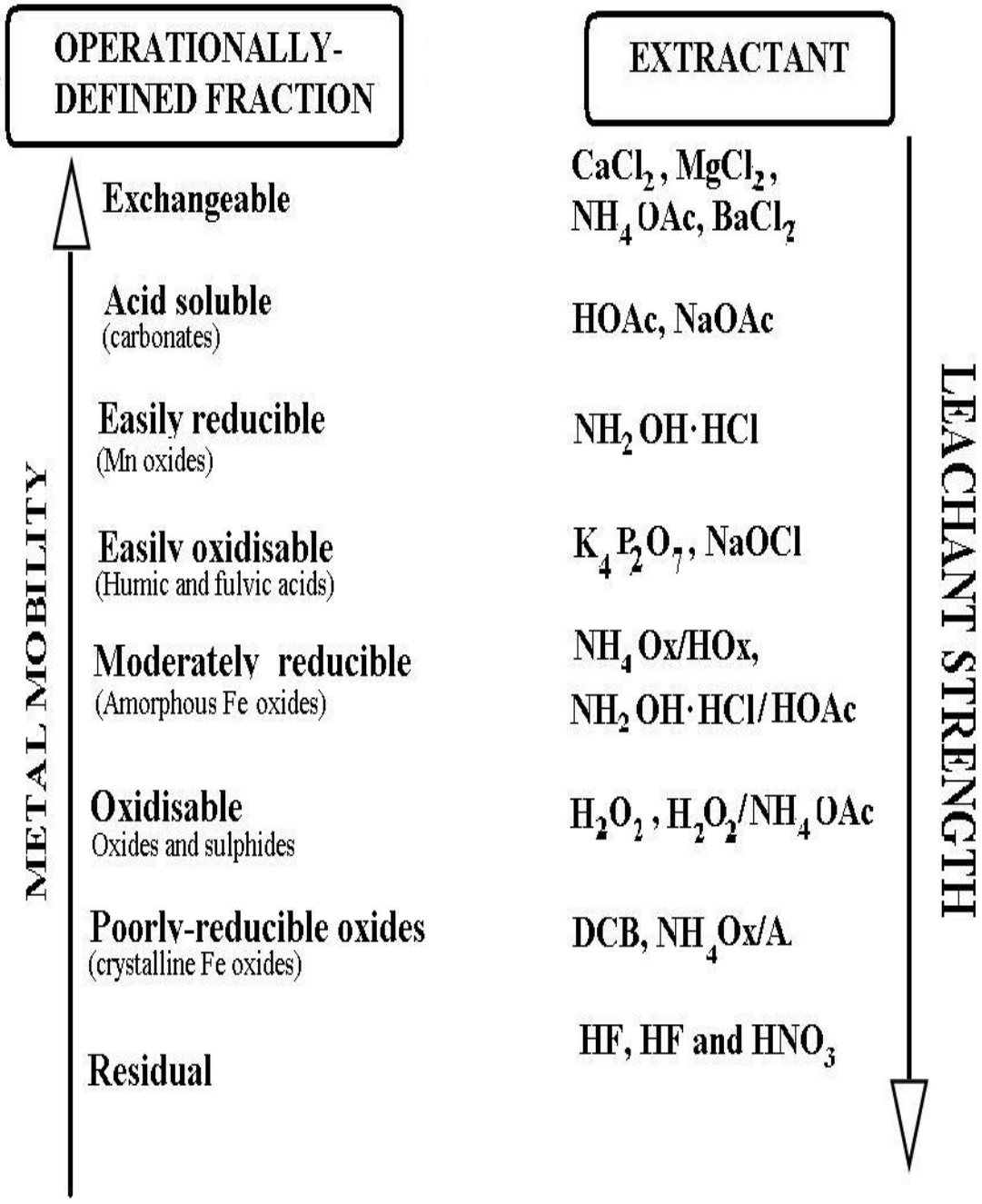



**Figure 2.2** Relationship between metal mobility in the different operationally-defined phases and extractant strength of common chemical reagents used for sequential extraction procedures (Filgueiras *et al.*, 2002).

**Table 2 3** Common sequential extraction procedures used to partition metals in environmental solid samples

| Protocol | Reagents | Fractions | Studied Samples |
|---|---|---|---|
| **Tessier *et al.*, (1979)** | 1 M $MgCl_2$ | Exchangeable | **Sediments** |
| | *Buffered 1 M NaOAc (pH 5)* | *Bound to Carbonates* | |
| | 0.04 M $NH_2OH{\cdot}HCl$ in 25% v/v HOAc | Reducible | |
| | *$H_2O_2$ in $HNO_3$ 0.02 M + 3.2 M $NH_4OAc$ in 20% (v/v) $HNO_3$* | *Oxidisable* | |
| | HF | Residual | |
| **BCR (1994)** | 0.11 M HOAc | Exchangeable/Carbonates | **Sediments** |
| | *0.5 M $NH_2OH.HCl$ acidified with 2 M $HNO_3$* | *Reducible* | |
| | 8.8 M $H_2O_2$ then 1 M $NH_4OAc$ (pH=2) | Oxidisable | |
| **Krishnamurti *et al.*, (1995)** | 1 M $Mg(NO_3)_2$ | Exchangeable | **Soils** |
| | *1 M NaOAc* | *Carbonate-bound* | |
| | 0.1 M $Na_4P_2O_7{\cdot}10H_2O$ | Metal-organic complex-bound | |
| | *0.1 M $NH_2OH{\cdot}HCl$ (in 0.01 M $HNO_3$)* | *Easily reducible metal oxide-bound* | |
| | $H_2O_2$(30%) + 0.02 M $HNO_3$ + 2 M $Mg(NO_3)_2$ in 20% $HNO_3$ | $H_2O_2$ extractable organic-bound | |
| | *0.2 M $(NH_4)_2C_2O_4$* | *Amorphous mineral colloid bound* | |
| | 0.2 M $(NH_4)_2C_2O_4$ / 0.1 M Ascorbic Acid | Crystalline Fe oxide-bound | |
| | *HF-HClO* | *Residual* | |
| **Davidson et al.,(2004)** | 0.11 M HOAc | Exchangeable/Carbonates | **Soils and Sediments** |
| | *0.2 M $(NH_4)_2C_2O_4$ adjusted to pH 3 by $HNO_3$* | *Reducible* | |
| | 8.8 M $H_2O_2$ followed by 1 M $NH_4OAc$ | Oxidisable | |
| | *Aqua Regia* | *Residual* | |

**Table 2.3(conts)** Common sequential extraction procedures used to partition metals in environmental solid samples

| Protocol | Reagents | Fractions | Studied Samples |
|---|---|---|---|
| **Miller *et al.*, (1986)** | 0.5 M $Ca(NO_3)_2$ | Exchangeable | **Soils** |
| | *0.44 M HOAc + 0.1 M $Ca(NO_3)_2$* | *Acid Soluble* | |
| | 0.01 M $NH_2OH{\cdot}HCl$ + 0.1 M $HNO_3$ | Mn oxide occluded | |
| | *0.1 M $K_4P_2O_7$* | *Organically bound* | |
| | 0.175 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$ | Amorphous Fe oxide occluded | |
| | *0.175 M $(NH_4)_2C_2O_4$ + 0.1 M $H_2C_2O_4$ under UV radiation* | *Crystalline Fe oxide occluded* | |
| | Aqua Regia + HF | Residual | |
| **Ahnstrom and Parker (1999)** | M $Sr(NO_3)_2$ | Soluble-exchangeable | **Soils** |
| | *buffered 1 M NaOAc (pH 5)* | *Sorbed-Carbonate* | |
| | 5 % NaOCl adjusted to pH 8.5 by HCl | Oxidisable | |
| | *0.2 M $H_2C_2O_4$ + 0.2 M $(NH_4)_2C_2O_4$ +0.1 M Ascorbic acid adjusted to pH 3 with $NH_4OH$* | *Reducible* | |
| | Aqua Regia | Residual | |

The BCR protocol has been criticised because, apparently, it lacks reproducibility (Sahuquillo *et al.,* 1999; Margui *et al.,* 2004). Consequently there have been numerous modifications to this protocol. The following sections will review the reagents and reaction conditions used in the BCR sequential extraction protocol, considering their advantages and disadvantages.

2.4.1 The acid-soluble fraction

The first step of the BCR sequential extraction uses 0.11 M acetic acid (HOAc) to extract the acid-soluble metals. The use of this reagent is intended to solubilise the carbonates which are unstable under acidic conditions. There are two aspects worth noting in this step. The first consideration is that water soluble and exchangeable

pollutants are determined together with the acid-soluble pollutants. The appropriateness of simultaneous determination of these fractions is questionable as exchangeable elements are thought to be closely related to plant uptake (Shuman, 1978; Kaasalainen and Yli-Halla, 2003; Lu *et al.*, 2005). It is thus proposed that this protocol serves as a compromise between analysis time and the amount of information obtained (Perez-Cid *et al.*, 1996).

The second aspect is the use of an organic acid (acetic acid) which is also used in TCLP extraction. The concentration of acetic acid in the TCLP extraction is 0.1 M. This raises the question of whether or not the results from 0.11 M HOAc extraction can be used to predict leaching of pollutant from a waste in landfill. Some researchers have already indicated the importance of determining the acid-soluble fraction (using 0.11 M HOAc) in landfilling of alkaline fly-ash (Van Herck and Vandecasteele, 2001). However there are no studies that compare the results from using both TCLP and 0.11M HOAc extraction (as part of BCR SEP). Nevertheless, based on the concentration of these two solutions, no significance difference is expected between the results of the TCLP (the one with pH 2.88 ± 0.05) and the 0.11 M HOAc (from BCR sequential extraction). This would imply that the results of the TCLP extraction and the first step of the BCR sequential extraction are the same for alkaline materials.

The original BCR protocol uses 40 ml of 0.11 M HOAc to extract 1 g of material at room temperature for 16 hours. The efficiency (extraction capacity) of this reagent has been questioned and thus higher concentrations of 0.43 M, 0.44 M and 0.5 M HOAc have been used as alternatives (Miller *et al.*, 1986; van Herck and Vandecasteele, 2001; Kaasalainen and Yli-Halla, 2003; Sahuquillo *et al.*, 2003; Peijnenburg *et al.*, 2007). Increase in acidity of HOAc (from 0.11 to 0.43 M) was found to increase the extractability of Pb and Cr but had no effect on Cu and Ni (Sahuquillo *et al.*, 2003). This effect was attributed to the higher capacity of 0.43 M HOAc to dissolve carbonates. To improve the extractability of elements using 0.11 M HOAc, other studies have adjusted the solution pH to 2.5 and 7.0 (van Hullebusch *et al.*, 2005; Virkutyte *et al.*, 2005; Álvarez-Valero *et al.*, 2009). The comparisons between the original protocol

and the modified versions have not been made and original protocol is still used in many current studies as it is a recognised standard protocol.

An alternative to 0.11 M HOAc is 1 M sodium acetate (NaOAc, buffered with HOAC to pH 5; Tessier *et al.*, 1979). The extraction with NaOAc has an advantage of using a shorter extraction time (5 hrs) compared to that of the BCR protocol (16 hrs). The buffered acetate reagent has also been reported to be more selective as it dissolves carbonates and dolomite without dissolving organic matter, Fe-Mn oxides, and aluminosilicates (Filgueiras *et al.*, 2002). Unbuffered acetic acid, on the other hand, is less specific and results in the dissolution of some silicates (Gleyzes *et al.*, 2002). However, results from Mester *et al*. (1998) show that there were no significant differences in the concentration of Cd, Cr, Cu, Ni, and Zn extracted by 0.11 M HOAc and by the sum of exchangeable and NaOAc extractable elements in sediments. The sum of exchangeable and NaOAc extractable Pb, in the same study, was higher than that extracted by 0.11 M acetic acid. Similar findings have been reported by van Hullebusch *et al*. (2005) where sum of exchangeable and NaOAc extractable Co, Fe, Mn, and Ni, were higher than those extracted by 0.11 M HOAc in anaerobic granular sludge. This could arise from three factors namely: the concentration of NaOAc is higher than that of HOAc; NaOAc has higher buffering capacity; and there could be a successive dissolution of $FeCO_3$ and $MnCO_3$ when NaOAc is applied after $MgCl_2$ (Tessier *et al.*, 1979; van Hullebusch *et al*., 2005). Further research is needed which will determine which extractant can best estimate the acid-soluble fraction.

### 2.4.2 The reducible fraction

The reducible fraction of the BCR sequential extraction is determined using 0.1 M hydroxylammonium chloride (HAC) adjusted to pH 2. This extraction is aimed at dissolving Fe-Mn oxides which are thermodynamically unstable under reducing conditions. This step is significant because Fe-Mn oxides are excellent scavengers of heavy metals and can immobilise a substantial amount of pollutants (Chao, 1972; Chao and Zhou, 1983; van Herck and Vandecasteele, 2001). These oxides play an important role in the mobility of pollutants in the environment (Neaman *et al.*, 2004a;

Silveira *et al.*, 2006). The dissolution of these oxides suggests that chemisorbed pollutants will be released into the soil solution.

The ideal reagent for the evaluation of pollutants associated with the oxides should contain a reducing reagent and a ligand (such as acetate and oxalate ions) to retain released ions in a soluble form. The extraction efficiency of the reagent is determined by its reduction potential and its ability to dissolve different crystalline forms of Fe and Mn oxyhydroxides (Tessier *et al.*, 1979; Shuman, 1982; Gleyzes *et al.*, 2002).

Hydroxylammonium chloride is a reducing reagent ($E^0$= –1.87 V) and its ability to dissolve the different metallic oxides depends on pH, concentration, extracting time and temperature (Gleyzes *et al.*, 2002). A solution of 0.1 M HAC (pH=2) dissolved on average 85% of manganese oxides and about 5% of iron oxides from various sediments after equilibrating for 30 minutes to six hours (Chao,1972; Gleyzes *et al.*, 2002). This reagent (extraction for 16 hrs) is associated with pronounced variability due to reduced buffering capacity of the reagent at pH 2 (Sahuquillo *et al.*, 1999; Sahuquillo *et al.*, 2003). Consequently, use of 0.5 M HAC (pH=1.5) has been employed (Sahuquillo *et al.*, 1999; Kaasalainen and Yli-Halla, 2003; van Hullebusch *et al.*, 2005; Kim and McBride, 2006; Cappuyns *et al.*, 2007). The modified reagent has been reported to provide increased extractability of pollutants and an improved reproducibility (Table 2.4). This modification appears to result in a reduced amount of heavy metals being extracted in the oxidisable fraction (Rauret *et al.*, 1999; Sutherland and Tack, 2003).

Ammonium oxalate (0.2 M, pH 3) has been proposed as an alternative to extract pollutants occluded by Fe-Mn oxides (Davidson *et al.*, 2004). This reagent has been used to dissolve both manganese and iron oxides (Shuman, 1982; Chao and Zhou, 1983). Davidson *et al*. (2004) observed higher extractability of Fe and Cu, when comparing 0.2 M ammonium oxalate (pH 3) to 0.5 M HAC (pH 1.5) in waste treated soils. Manganese and Zn extractability were not affected by the reagent used except in iron oxide-rich soils where ammonium oxalate extracted more Zn. However, the use of this reagent in the determination of Ca and Pb is discouraged because sparingly soluble

Ca/Pb oxalate salts are formed resulting in low recoveries of Ca and Pb in solution (Davidson *et al.*, 2004).

**Table 2.4** A comparison between 0.1 M and 0.5 M hydroxylyammonium chloride (HAC) in extracting Cd, Cr, Cu, Ni, Pb, and Zn from CRM 601 (sediment reference material). The original BCR protocol uses 0.1 M HAC and the modified protocol uses 0.5M HAC (Rauret *et al.*, 1999)

| ***Extractant*** | ***Cd*** | ***Cr*** | ***Cu*** | ***Ni*** | ***Pb*** | ***Zn*** |
|---|---|---|---|---|---|---|
| | **(mg $kg^{-1}$)** | | | | | |
| **0.1 M HAC** | 3.09 ± 0.88 | 1.42 ± 0.79 | 7.87 ± 5.14 | 5.55 ± 1.42 | 37.3 ± 7.7 | 175 ± 15 |
| **0.5 M HAC** | 3.95 ± 0.53 | 10.6 ± 0.9 | 72.8 ± 4.9 | 10.6 ± 1.3 | 205 ± 11 | 266 ± 17 |

Incomplete dissolution of Fe-Mn oxides can result in readsorption of released pollutants. Readsorption of released pollutants can be minimised by using strong complexing agents. Complexing agents such as acetate, oxalate, and ascorbate ions are often employed for this purpose (Tessier *et al.*, 1979; Shuman, 1982; Chao and Zhou, 1983; Gleyzes *et al.*, 2002). Oxalate ions form stable complexes with Al (log K = 15) and Fe (log K ranging between 4.35 and 18.49 for $Fe^{3+}$, and between 3.20 and 5.15 for $Fe^{2+}$). However, as previously cautioned, oxalate ions may form sparingly soluble Ca/Pb salts thus leading to underestimation of their availability or solubility (Gleyzes *et al.*, 2002; Davidson *et al.*, 2004).

2.4.3 The oxidisable fraction

The oxidisable fraction, particularly for soils and sediments, refers to the elements bound to organic matter. Reduced species such as sulphides are also included in the oxidisable fraction. This fraction is important because under oxidising conditions organic matter, and other reduced species, are degraded, leading to the release of retained pollutants. Hettiarachchi *et al.* (2003) indicated that the measurement of the oxidisable fraction is essential in land application of sewage sludge. A number of

reagents are used to estimate the oxidisable fraction because of the dynamic nature of this target phase.

The oxidisable fraction in the BCR sequential extraction is determined by digestion at 85°C using 8.8 M $H_2O_2$ followed by $NH_4OAc$ (pH 2) extraction at room temperature. Hydrogen peroxide is an oxidising agent (E°=1.77 V) and has been used to oxidise organic matter and sulphides (Tessier *et al.*, 1979; Pueyo *et al.*, 2007). This reagent has been criticised due to incomplete dissolution of organic matter and partial attack of silicates. It does however; represent a compromise between complete oxidation (of organic matter and sulphides) and minimal alteration of the silicates (Filgueiras *et al.*, 2002; Gleyzes *et al.*, 2002). Decreasing pH of this reagent improves dissolution of organic matter at the expense of selectivity, whereas increasing pH results in redistribution of extracted pollutants (Bermond, 2001). Furthermore, oxalic acid is released during the destruction of organic matter which dissolves iron oxides and causes secondary precipitation of sparingly soluble oxalates (Gleyzes *et al.*, 2002). To overcome these difficulties Rauret (1998) suggested that $H_2O_2$ would be more effective in dissolving organic matter when applied after the reducible fraction is removed.

Other studies have used sodium hypochlorite (NaOCl) and sodium pyrophosphate ($Na_4P_2O_7$) instead of $H_2O_2$ to estimate the elements which are retained on organic matter (Shuman, 1983; Titshall, 2003). Because NaOCl is a stronger oxidizing agent (E°=0.90V) than $Na_4P_2O_7$, it is preferred (Ahnstrom and Parker, 1999; van Herck and Vandecasteele, 2001; Filgueiras *et al.*, 2002). The extraction with NaOCl (pH 9.5) is efficient and it has been said to cause minimal dissolution of the silicates (Shuman, 1983; Filgueiras *et al.*, 2002; Wilson *et al.*, 2006). However, this reagent may precipitate released cations and/or oxidise Mn oxides to $MnO^{4-}$ ions (Gleyzes *et al.*, 2002; Mikutta *et al.*, 2005). When reviewing the removal of organic matter from soils Mikutta *et al*. (2005) concluded that NaOCl was more effective in removing organic matter than $H_2O_2$.

## 2.5 Conclusions

It is clear that no single chemical extraction method is suitable for all environmental samples (i.e. soils, wastes, and sediments) encountered. The most suitable method should depend upon the purpose for which the test is conducted; the material being studied, and the elements of interests. The purpose of the tests is related to what mechanism causing the release of pollutant is being assessed (i.e. leaching, plant uptake, or partitioning of elements) and environmental conditions (such production of organic acids and changes in solution chemistry). The material being studied covers the type of material (waste, soil, sediment, or contaminated soil) and mineralogy (such carbonates, crystalline Fe oxides, and/ or organic matter). Factors affected by the material being studied are choice of reagent (extracting solution), ionic strength and the pH of the extracting solution, extraction time, and liquid-to-solid ratio. Wrong decision with regards to these factors will results in under/overestimation of elements availability due to saturation of the extracting solution; incomplete dissolution of targeted phases; partial attack of non-targeted phases; and formation of secondary precipitates. The elements of interest will influence the choice and the acidity of the extracting reagent. Firstly, labile elements (such as Cd and Zn) seem to be unaffected by increase in acidity while the extractability of elements with low mobility (such as Cu, Ni, Pb, and Cr) increases with increasing acidity. Secondly, some elements form secondary precipitates with anions of extracting solution (such Ca and Pb with oxalate ion). Hence, the multiplication of chemical extraction methods is inevitable. However, there are reagents which can be used for assessing releasing of pollutant for different purposes (like HOAc used in the BCR sequential extraction). Further research is required to help in understanding the effect of time in chemical extraction methods; optimising extraction methods for different conditions for which they developed; and comparability between different extraction methods.

# CHAPTER 3

# THE CHARACTERISATION OF ELECTRO-WINNING WASTE, SMELTER SLAG, AND INANDA SOIL FORM

## 3.1 Introduction

The properties of soils and wastes will determine the potential for land application of a waste and several authors have noted the importance of determining the soil and waste properties for land application of wastes (Overcash and Pal, 1979; Miller and Miller, 2000). The characterisation of waste materials prior to their disposal provides information about the potential impacts to the environment when the waste is applied to a soil. The soil and waste chemical properties frequently considered include pH, electrical conductivity (EC), cation exchange capacity (CEC), extractable elements, and mineralogy (Overcash and Pal, 1979; Miller and Miller, 2000). Determining soil and waste properties also provide some indication of possible interactions between the soil and waste that may results in both mobilisation and immobilisation of pollutants. For instance waste materials with high pH (10-13) may dissolve organic matter and can results in the release of heavy metals (Cameron *et al.*, 1997). Whereas, the presence of Mn, Al, and Fe oxides in soils may reduce heavy metals and P leaching when manures are applied to soils (Codling and Isensee, 2005).

The basic physiochemical properties of soils and wastes may also influence the choice of extracting reagent in chemical extraction methods (Chapter 2) as these properties affect the concentration of the elements extracted from the waste or soil using different extracting reagents. For instance high pH of a waste or soil can reduce the concentration of the elements extracted. Bermond (2001) reported that the concentration of an element extracted is affected by the solution composition during extraction. Furthermore, crystalline minerals may also be partially dissolved by some reagents. Thus a clear understanding of the reactions and interaction between the reagent and the material being extracted is important as waste management decisions are taken based on the results obtained from the extractions.

The aim of this chapter is to review the characteristics of the Mn-rich smelter slag (SS), the Mn-rich electro-winning waste (EW), and the A horizon of the Inanda soil form (Ia) that were selected for use in this study. The characteristics of these materials will be discussed with the implication for land disposal and chemical extraction methods. The properties considered include basic physical and chemical properties, mineralogy and extractable elements. Many of the physical and chemical properties of these materials (except mineralogy and the analysis on the electron microscope) were determined by others prior to commencement of this study (BHP-Billiton report, 2005; Titshall, 2007). These data are presented here and discussed in order to assist with an understanding of important aspects pertinent to this particular study.

## 3.2 Materials and methods

Material collection and preparation

Materials were previously collected and characterised (BHP-Billiton report, 2005; Titshall, 2007). The collection and characterisation of the materials is repeated here for clarity and completeness. Two manganese-rich wastes, a smelter slag (SS) and an electro-winning waste (EW) were collected from the processing plants prior to their disposal on dedicated disposal sites (Figure 3.1). The SS is the residue produced after Mn-rich ores are smelted in an arc-furnace with added flux materials (lime and silica). After the reduced Mn product is separated, the molten slag is allowed to solidify, crushed and disposed of on a dedicated slag disposal heap. The EW is the by-product produced after Mn-rich ores are milled, solubilised in acid and Mn retrieved using electroplating. Conditioners (lime and ammonia sulphate) are added during the electrolytic recovery process. The residual material (from electrolytic recovery) is dewatered by a belt press and the filter cake disposed of to a dedicated disposal site.

The A horizon of an Inanda soil form (Ia, Soil Classification Working Group, 1991) was collected from land under forestry at World's View (Hilton, KwaZulu-Natal). This soil is an organic rich acidic soil and was chosen because it represents a typical soil on which these wastes (SS and EW) can be applied. The SS, EW, and Ia soil were all air-dried, milled to pass through a 2 mm sieve and stored in black plastic bins for further use. The charecterisation is presented in Appendix 3.1.

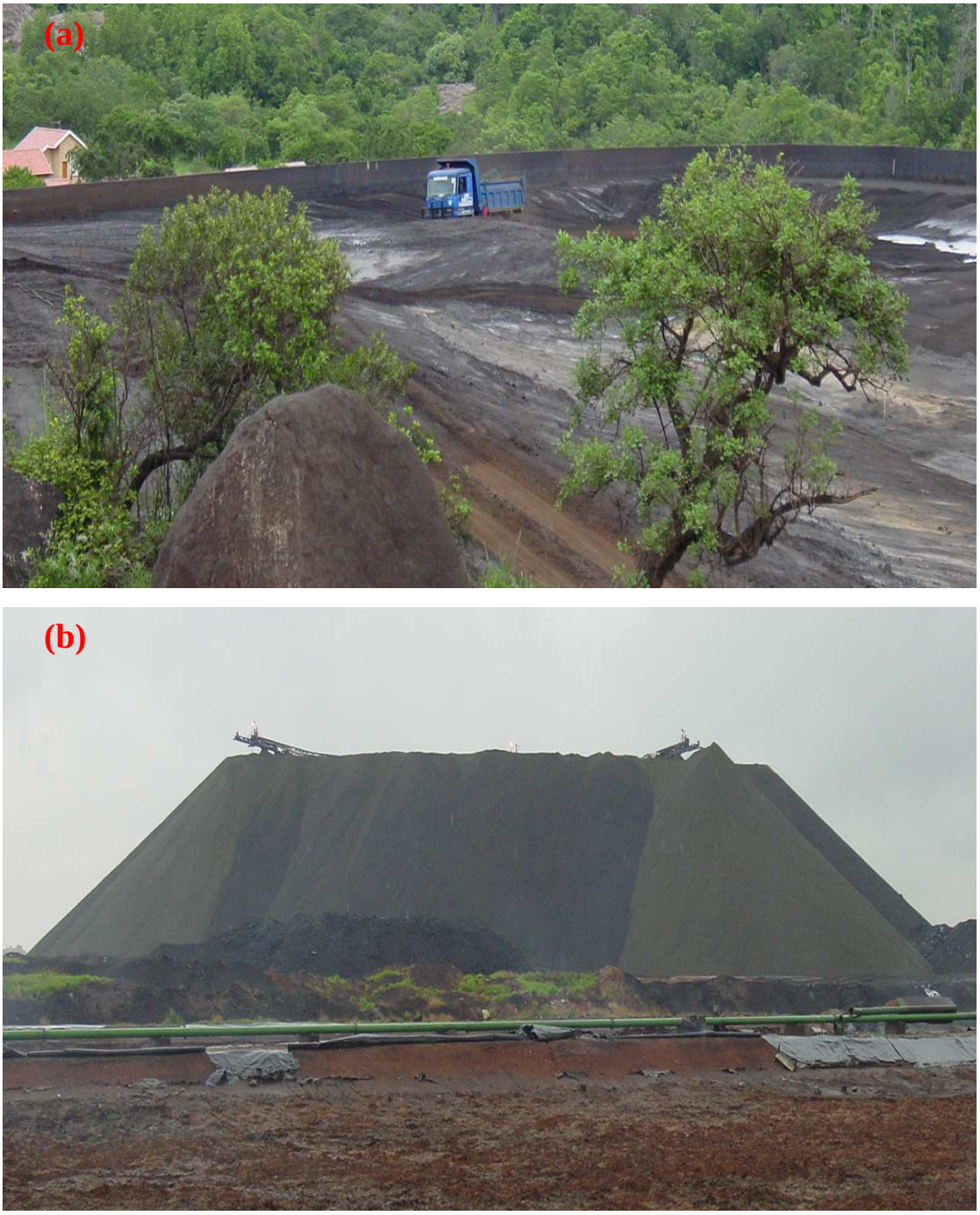



**Figure 3.1** The (a) electro-winning (EW) waste disposal site (Pappas Quarry, Nelspruit, Mpumalanga, South Africa), showing a view overlooking the quarry and (b) smelter slag-heap at Samancor property (Meyerton, Gauteng, South Africa).

## 3.3 Results and Discussion

### 3.3.1 The electro-winning waste properties

#### *3.3.1.1 Basic properties and mineralogy*

The EW is characterised by a high total content of Fe and Mn (Table 3.1 and Figure 3.1 b), occurring in a ratio of approximately 2:1 (Fe:Mn). It has a near neutral pH ($pH_{water}$ 6.89), a high EC (1735 mS $m^{-1}$), and a low organic carbon (0.56 g $100g^{-1}$) content (Table 3.1). The high EC of the EW is due to a high concentration of soluble salts in the waste. This is supported by the high concentrations of soluble Ca, Mn, Mg, S, and Na determined in saturated paste extracts (Table 3.2). The high concentration of S suggests that the soluble salts are present mainly as sulphates (Titshall, 2007).

The EW was leached with distilled water to analyse for the soluble component (Titshall, 2007). The resultant supernatant was evaporated to dryness at room temperature and the precipitates were analysed on the XRD. The XRD traces indicated that the soluble component was predominantly ammonium sulphates salts such as mohrite ($(NH_4)_2Fe(SO)_4.6H_2O$) and boussingaultite ($(NH_4)_2Mg(SO_4)_2.6H_2O$) (Titshall, 2007). Other minerals present as the soluble component were despujolsite ($Ca_3Mn^{4+}(SO_4)_2(OH)_6.3H_2O$) and ilesite ($(Mn,Zn,Fe^{2+})SO_4.4H_2O$). The presence of Mn (IV) and Fe (II) has implications for reducing and oxidising reagents used in sequential extractions (Appendix 3.2).

The surface characteristic of the EW was characterised by microporosity and high surface area (Figure 3.2). These surface characteristics corresponded to a cation exchange capacity (CEC) of 9.50 $cmol_c$ $kg^{-1}$ and high sum of extractable base cations (Table 3.1). The microporosity of the EW is expected to result in an increased dissolution rates. This has implication for time required to attain equilibrium during extraction.

The EW mineralogy is dominated by the oxides jacobsite ($MnFe_2O_4$) and magnetite ($Fe_3O_4$) (Appendix 3.3). There were smaller amounts of gypsum ($CaSO_4{\cdot}2H_2O$) and barite ($BaSO_4$). Although the presence of barite was not clear but high Ba and S content (Table 3.1) supports the presence of barite (Titshall, 2007).

**Table 3.1** XRF analysis and basic chemical characteristics of the smelter slag (SS) and electro-winning waste (EW; BHP-Billiton report, 2005; Titshall, 2007). The pH and EC were measured in 1:2.5 suspension

| Parameter | | SS | EW |
|---|---|---|---|
| **pH** | **$H_2O$** | 9.73 | 6.89 |
| | **1 M KCl** | 9.81 | 6.86 |
| **Electrical conductivity (25 $^oC$)** | **(mS $m^{-1}$)** | 35.8 | 1735 |
| **Organic carbon** | **(g $100g^{-1}$)** | 0.72 | 0.56 |
| **$NH_4^+$-N** | **(mg $kg^{-1}$)** | 6.32 | nd |
| **$NO_3^-$-N** | **(mg $kg^{-1}$)** | 2.90 | nd |
| **Total N** | **(mg $kg^{-1}$)** | 391 | 9246 |
| **Cation exchange capacity** | **($cmol_c$ $kg^{-1}$)** | 3.42 | 9.50 |
| **Extractable base cations ($cmol_c$ $kg^{-1}$)** | **Ca** | 13.2 | 71.0 |
| | **Mg** | 3.97 | 1.76 |
| | **Na** | 0.23 | 1.31 |
| | **K** | 0.22 | 0.06 |
| **Calcium carbonate equivalence** | **(%)** | 40.2 | 12.6 |
| **Major oxide content (%)** | **$SiO_2$** | 37.41 | 5.26 |
| | **$Al_2O_3$** | 4.83 | 1.11 |
| | **$Fe_2O_3$** | 0.79 | 37.89 |
| | **MnO** | 19.40 | 30.16 |
| | **MgO** | 7.61 | 0.57 |
| | **CaO** | 26.23 | 5.77 |
| | **$Na_2O$** | 0.13 | 0.00 |
| | **$K_2O$** | 0.16 | 0.00 |
| | **$TiO_2$** | 0.19 | 0.0490 |
| | **$P_2O_5$** | 0.01 | 0.14 |
| | **Total** | 96.76 | 80.95 |
| **Minor elements content (mg $kg^{-1}$)** | **S** | 14499.3 | 207955.5 |
| | **As** | 0 | 119 |
| | **Pb** | 2 | 839 |
| | **Zn** | 0.0 | 274.0 |
| | **Cu** | 0.0 | 264.8 |
| | **Ni** | 0.0 | 39.3 |
| | **Cr** | 0.0 | 0.0 |
| | **V** | 8.4 | 63.0 |
| | **Ba** | 2283.0 | 8221.4 |
| | **Sr** | 835.4 | 4446.4 |

*nd not determined.

**Table 3.2** Analysis of saturated paste extracts of the smelter slag (SS) and electro-winning waste (EW) (Titshall, 2007)

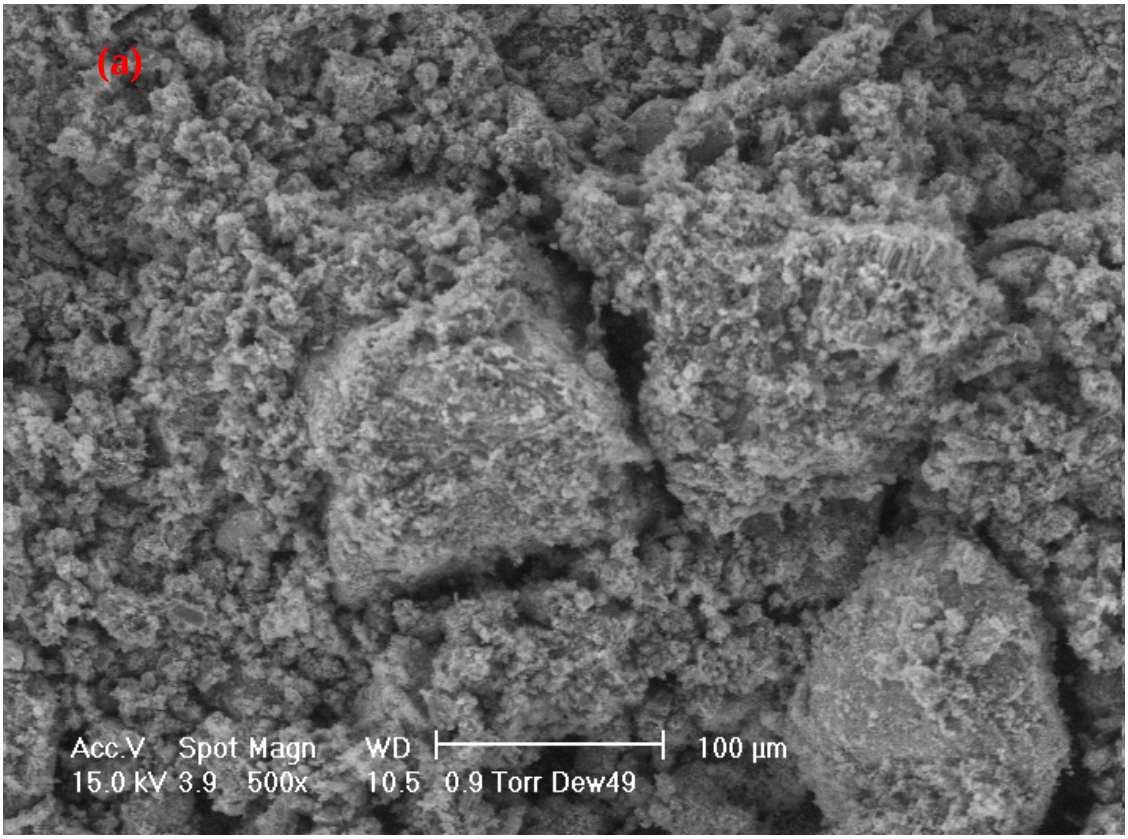
| Sample | Al | Ba | Cd | Co | Cr | Cu | Fe |
|---|---|---|---|---|---|---|---|
| | ----------(mg $L^{-1}$)---------- | | | | | | |
| **SS** | 3.33 | 0.14 | bd | bd | 0.01 | 0.12 | bd |
| **EW** | 0.03 | 0.05 | 0.01 | 71.70 | bd | 0.28 | 0.06 |
| | **Mn** | **Ni** | **P** | **Pb** | **S** | **Sr** | **Zn** |
| **SS** | 0.61 | bd | 0.25 | bd | 502 | 2.43 | bd |
| **EW** | 9835 | 10.8 | 0.07 | 0.73 | 31815 | 13.4 | 1.13 |
| | **Ca** | **Mg** | **Na** | **K** | **EC (mS $m^{-1}$)** | **SAR** | **SP (%)** |
| | ----------($cmol_c$ $L^{-1}$)---------- | | | | | | |
| **SS** | 2.56 | 0.03 | 1.12 | 0.13 | 244 | 0.99 | 17.7 |
| **EW** | 3.74 | 23.5 | 4.06 | 0.25 | 6780 | 1.10 | 50.0 |

bd below detection.
EC Electrical conductivity.
SAR Sodium adsorption ratio.
SP Saturation percentage.

The dissolution reactions and the dissolution constants (log $K_{dissolution}$) for magnetite and jacobsite are presented in equation 3.1 and 3.2, respectively (Lindsay, 1979; Blanc *et al*., 2007). The stability (Eh-pH) diagram for these mineral and other Fe and Mn minerals is presented in Figure 3.3. Both magnetite and jacobsite are dissolved at low pH and under reducing conditions (equation 3.1; 3.2 and Figure 3.3). The dissolution of these minerals may result in the release of Fe and Mn (Appendix 3.2).

$$Fe_3O_4 + 8H^+ \rightleftharpoons 3Fe^{3+} + e^- + 8H_2O \qquad \log K = -3.42 \quad \textbf{3.1}$$

$$MnFe_2O_4 + 6H^+ \rightleftharpoons 2Fe^{2+} + Mn^{2+} + 3H_2O + \tfrac{1}{2}O_2 \qquad \log K = -1.24 \quad \textbf{3.2}$$




**(b)**

| Element | Weight (%) |
|---|---|
| Mg | 0.52 |
| Al | 1.78 |
| Si | 4.60 |
| S | 5.14 |
| Ca | 4.21 |
| Mn | 30.15 |
| Fe | 53.88 |
| Total | 100.27 |

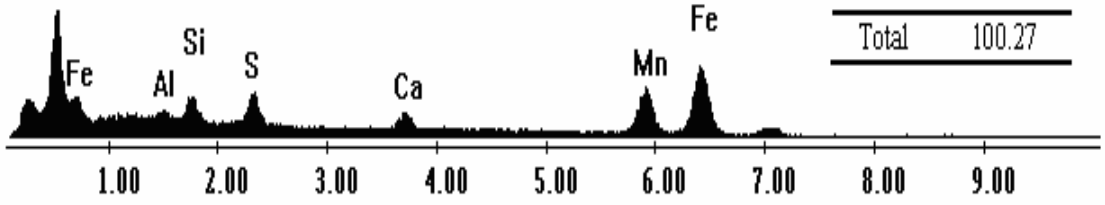



**Figure 3.2** (a) A scanning electron microscope image, (b) an EDX trace with a table indicating the composition of electro-winning waste.

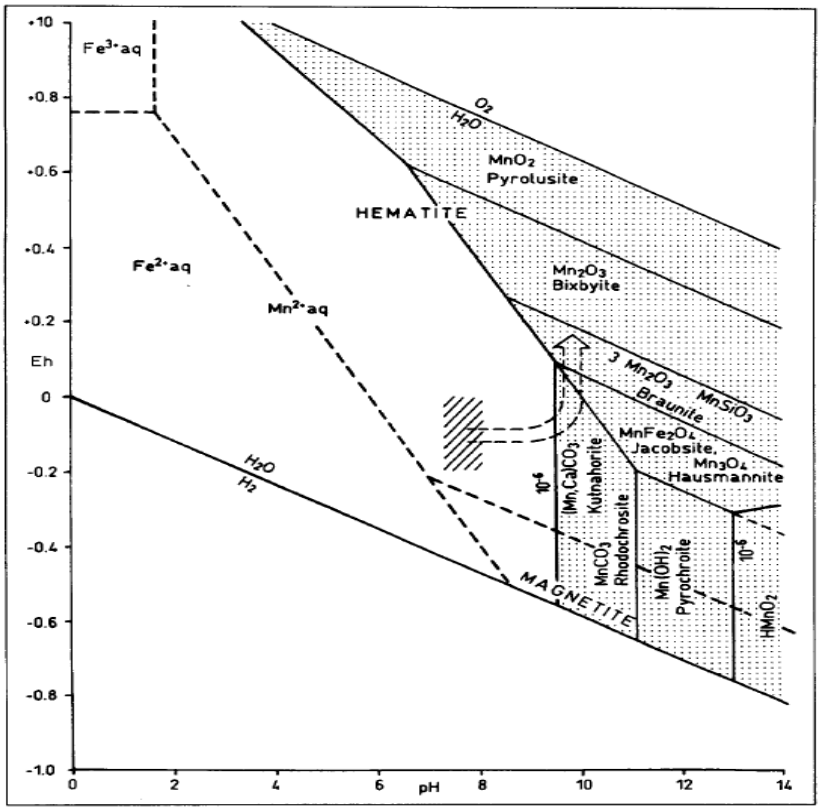



**Figure 3.3** The Eh-pH diagram for Fe and Mn species (Klemm, 2000).

*3.3.1.2 Dissolution investigation*

The EW has a moderate acid buffering capacity (Appendix 3.4). The initial equilibrating solution pH of 0.5, 1.00, and 3.00, when equilibrated with the EW, increased to 1.44, 3.37, and 6.22, respectively (Appendix 3.4). Above an equilibration pH of 6.22, the pH did not increase with increasing solution pH (Appendix 3.4) indicating a strong alkaline buffering capacity. This was not surprising as the EW is known to have acid producing capacity (Titshall, 2007). The alkaline pH was probably buffered by the release of $H^+$ ions from ammonium salts (equation 3.3).

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad \textbf{3.3}$$

Most elements in the EW decreased from equilibrium pH of 1.44 up to equilibrium pH of 6.22 (Figure 3.4). There was an increase in the concentration of Si from equilibrium pH 1.44 to 3.37 followed by a decrease (Figure 3.4 b) the reason for this is not clear.

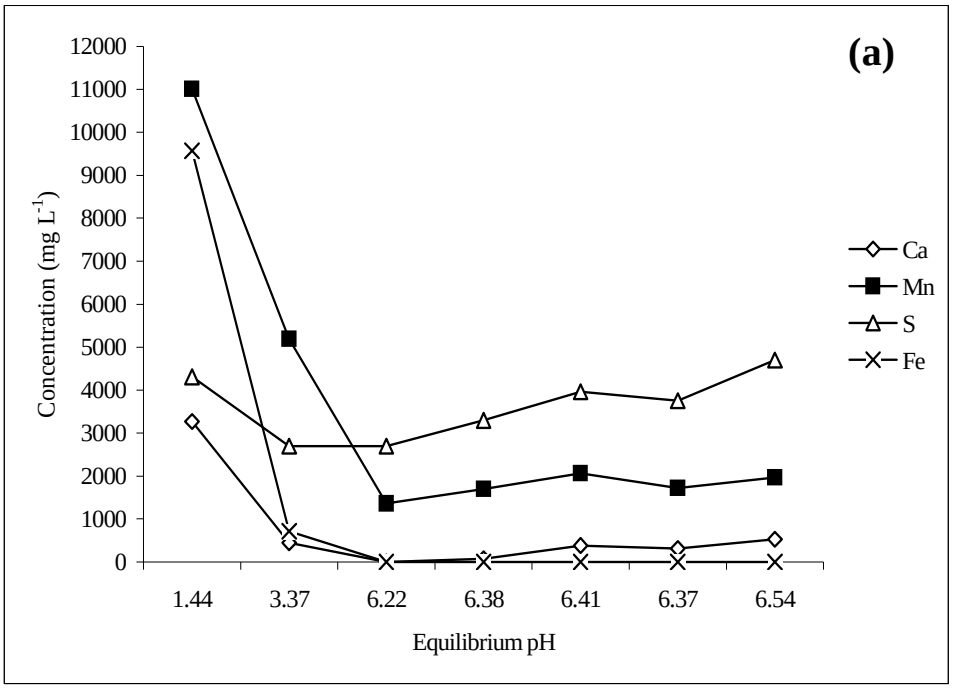
The concentrations of Fe, Ca, Al, Si, and Pb were very low at pH > 6. This indicates that most elements had higher solubility at low pH. The concentration of Fe and Mn were higher and followed the same trend (Figure 3.4 a). The trend which was followed by Fe and Mn might be indicating the dissolution of jacobsite and magnetite with varying pH solutions. These results suggest that the release of Fe, Ca, Al, Si, and Pb from the EW is pH dependent. Consequently, higher concentrations of these elements will be extracted by a low pH extracting solution.

Sulphur and Mg behaved differently compared to other elements showing a more consistent concentration regardless of the pH. The concentration of these two elements decreased from equilibrium pH 1.44 to 3.37 then increased until equilibrium pH of 6.41. It was also noted that the concentration of these elements was lower than those in saturated paste extract (2850 mg $L^{-1}$ for Mg and 31815 mg $L^{-1}$ for S). These two elements existed as soluble (most likely as $MgSO_4$) and possibly as exchangeable elements. The soluble salts and exchangeable elements are not affected by the pH of the extracting solution. This suggests that the release of Mg and S from the EW is independent of the pH. Their concentration was lower than those of saturated paste extract probably due to dilution effect.

*3.3.1.3 Adsorption behaviour*

The EW has exceptionally high P sorbing/fixing potential that tends towards an H-type curve (Figure 3.5). The H-type curve is adsorption isotherm that indicates high affinity of the adsorbent for the adsorbate at low to moderate surface coverage (McBride, 1994).

Therefore the steep slope implies high affinity of the mineral phases (jacobsite and magnetite) for P. These results were not surprising as oxides, particularly Fe, Mn, and Al, have high P-fixation capacity (Stone and Morgan 1984; Schwertmann and Taylor, 1989). The removal of P from solution may be a result of adsorption of P on jacobsite and magnetite surfaces and/or formation of Fe and Mn phosphates. Titshall (2007) proposed that other P-removing mechanism such as secondary precipitation of Ca, Fe, and Mn phosphate minerals may have contributed to the observed P-sorption capacity of the EW.



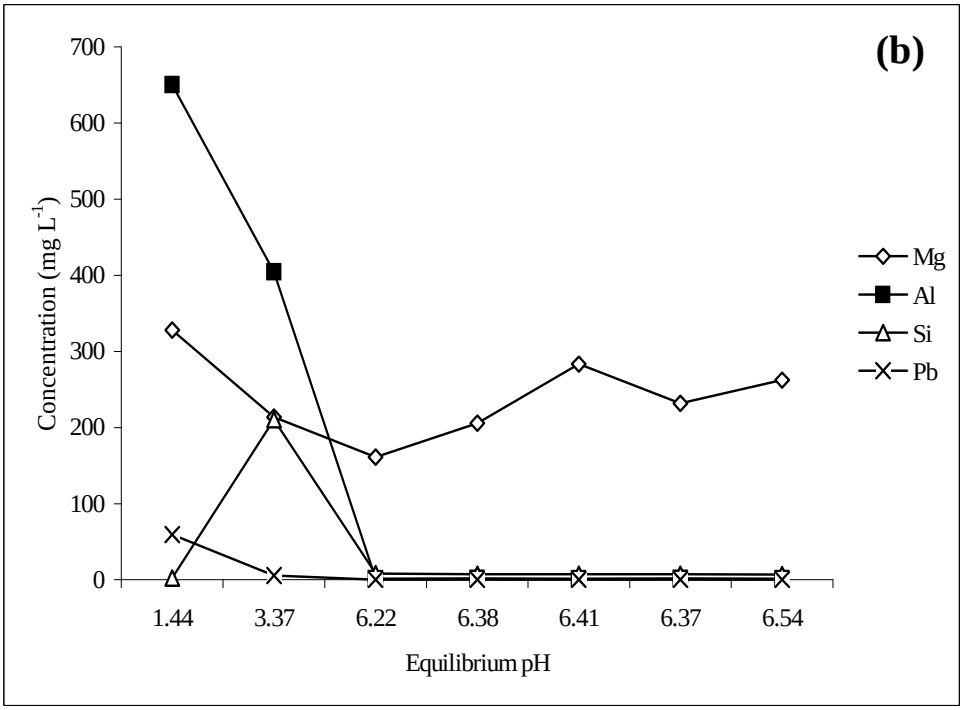




**Figure 3.4** Concentrations of (a) Ca, Mn, S and Fe and (b) Mg, Al, Si, and Pb in solution after the electro-winning waste was treated with solutions of known pH (BHP-Billiton report, 2005).

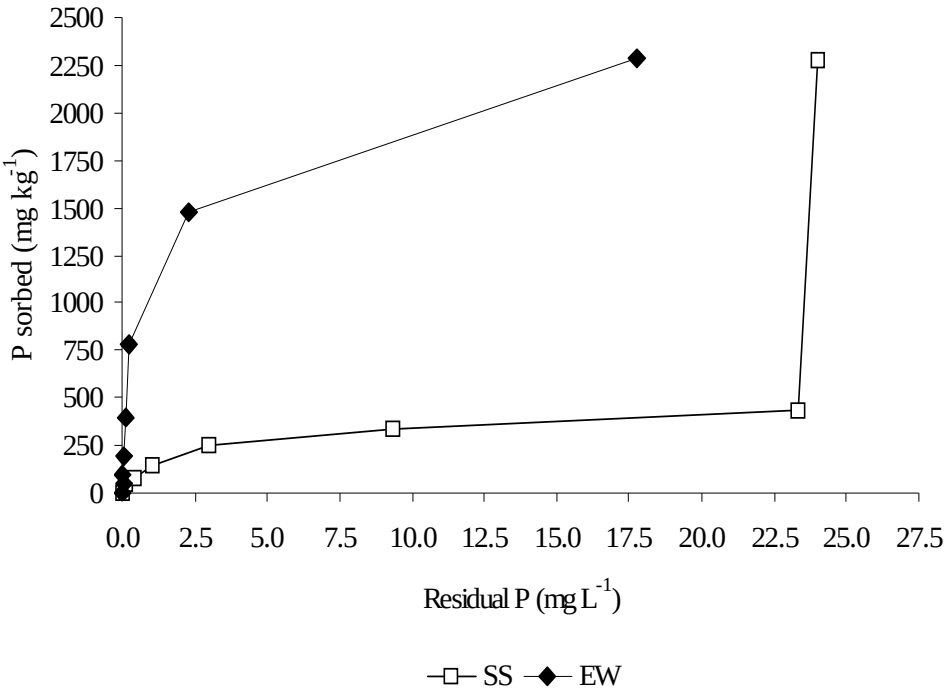



**Figure 3.5** Phosphorus sorption isotherms for smelter slag (SS) and electro-winning waste (EW; Titshall, 2007)

The high P-fixing capacity of the EW suggests that the EW can remove elements that generally undergo specific adsorption on oxide surfaces such Cr, As, Se, and V. Several authors have indicated that jacobsite can be used to remove Cr and As from solution (Hu et al., 2005; Parsons et al., 2009). Jacobsite, like $MnO_2$, can oxidise V and Se (Bartlett, 1986).

The EW also showed high affinity for Zn, Cu, and Ni (Figure 3.6). The sorption of Cu on EW can be described by an H-type curve, whereas that of Ni and Zn can be described by an L-type curve (Figure 3.5). Both H-type and L-type curve indicate high affinity of the adsorbent for the adsorbate at lower solution concentration. Iron and Mn oxides have been known to be excellent scavengers for heavy metals (Chao, 1972; Chao and Zhou, 1983; van Herck and Vandecasteele, 2001). Thus, the sorption of these heavy

metals on EW suggests a high of affinity jacobsite and magnetite for heavy metals and the potential for EW to immobilise heavy metals.

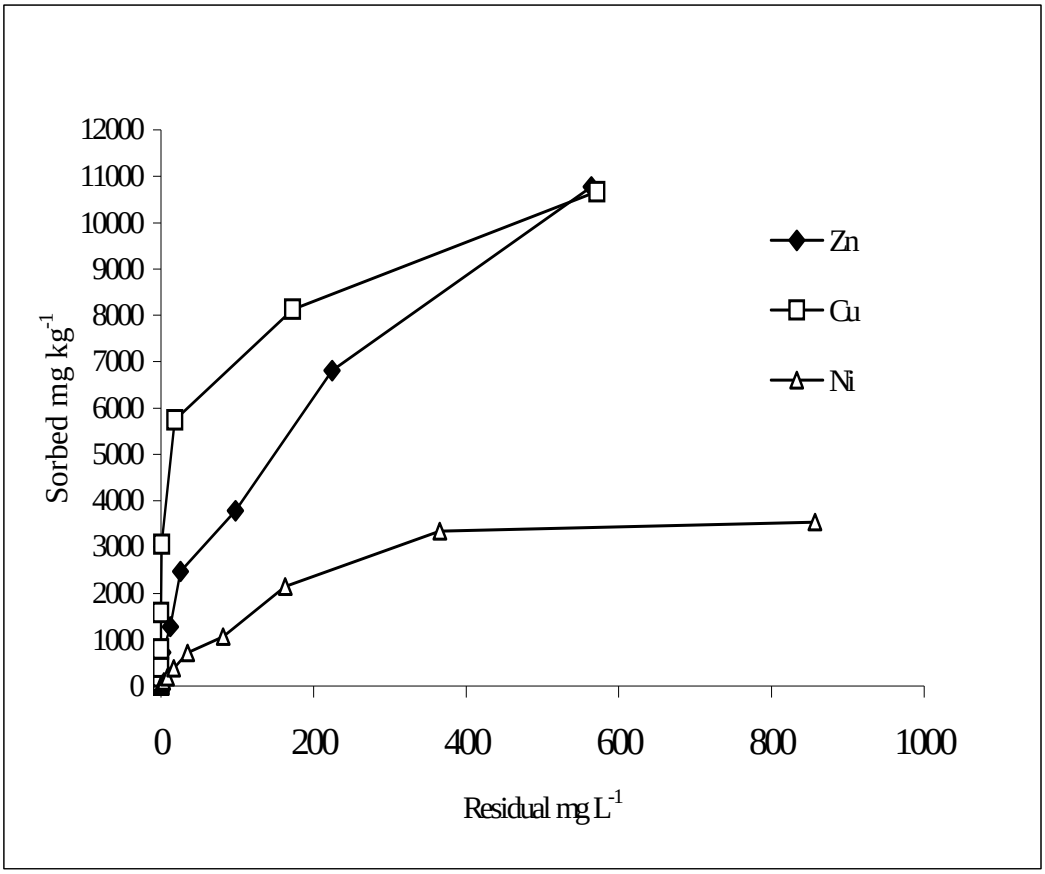



**Figure 3.6** Zinc, Ni and Cu sorption isotherm of the electro-winning waste (BHP-Billiton report, 2005).

3.3.2 The smelter slag properties

*3.3.2.1 Basic properties and mineralogy*

The SS has a high total content of Ca, Mn, and Si (Table 3.1 and Figure 3.7b) which occurred in the ratio of approximately 1.4: 1: 1 (Ca: Mn: Si). The SS is also characterised by an alkaline pH ($pH_{water}$ 9.73), a high calcium carbonate equivalence (CCE, 40.2%), low OC content (0.72 g $100g^{-1}$), and a low EC (Table 3.1). The low EC (35.8 mS $m^{-1}$) of the SS suggests low content of soluble salts which was confirmed by low content of soluble elements in the saturated paste extract (Table 3.2). The surface characteristic of the SS has low surface area and, unlike the EW, there was a lack of

microporosity (Figure 3.7a). Consequently, the CEC (3.42 $cmol_c\ kg^{-1}$) and sum of extractable base cations of the SS were lower than those of the EW (Table 3.1). The surface characteristic of the SS can result in slow dissolution of the solid phases.

Mineralogical analysis showed that the SS is dominated by Ca-Mn silicate olivine (glaucochroite, $(Ca, Mn)_2SiO_4$)) (Appendix 3.5). Small quantities of bustamite $CaMn(SiO_3)_2$, quartz, lime (CaO), and possibly gypsum were also identified.

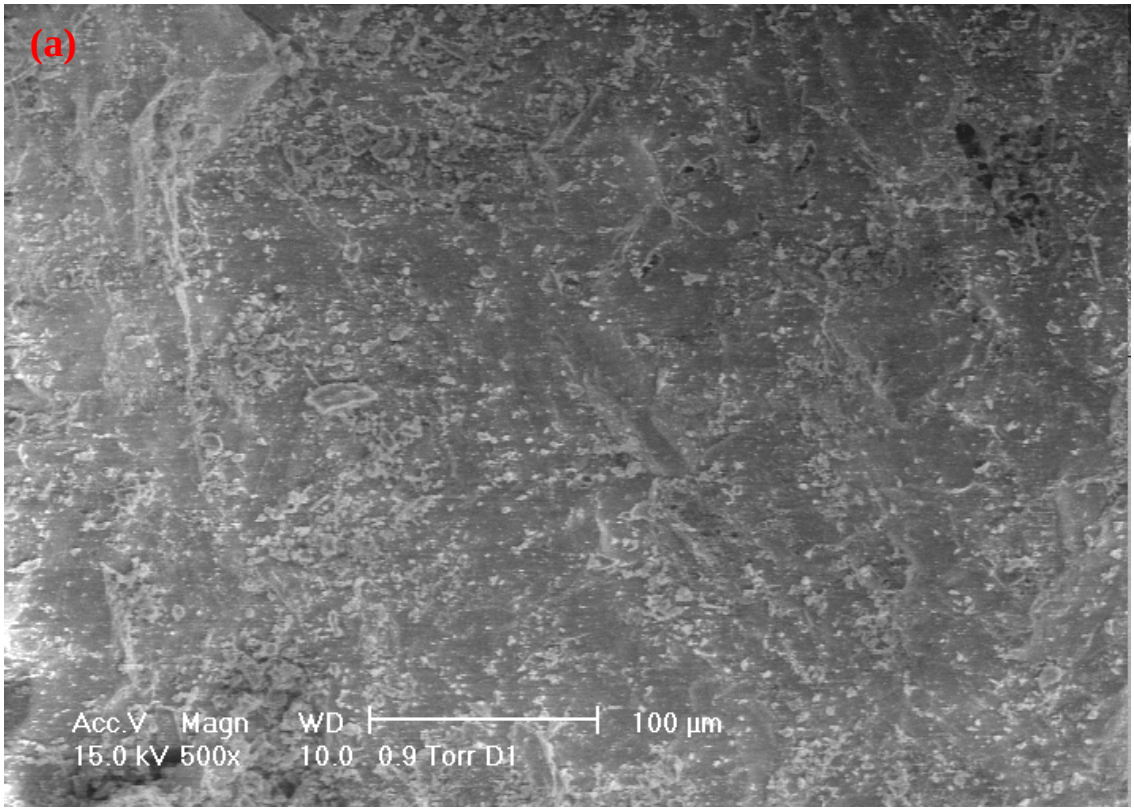
The dissolution reaction and dissolution constant ($\log K_{dissolution}$) of olivine is presented by equation 3.4 (Lindsay, 1979). Olivines are expected to dissolve at low pH and in the presence of organic acids. Hence, glaucochroite is expected to dissolve under these conditions and release Ca, Mn and Si (Appendix 3.6).

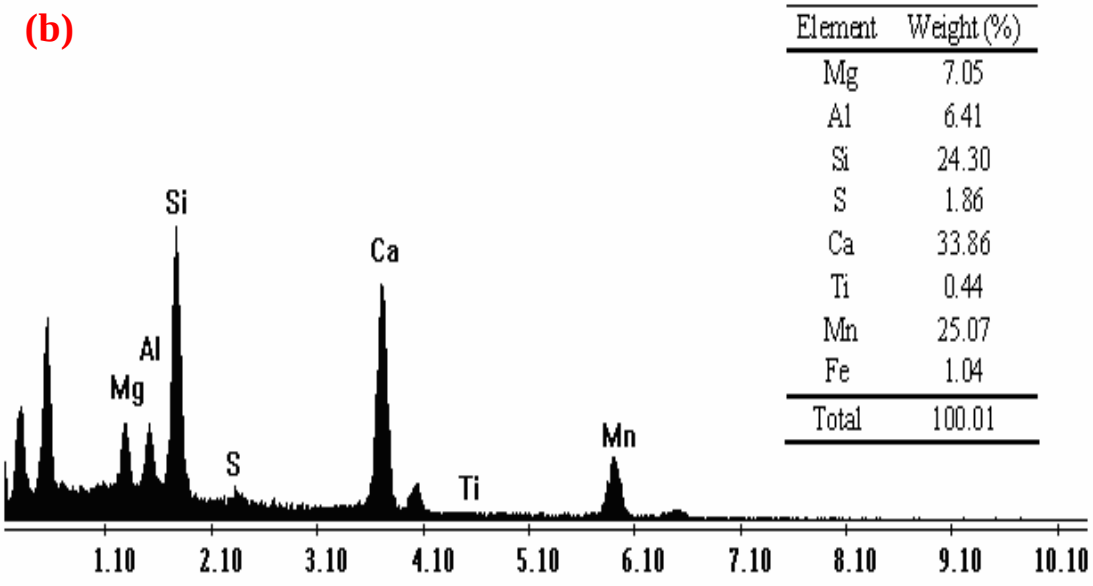
$$Ca_2SiO_4 + 4H^+ \rightleftharpoons 2Ca^{2+} + H_4SiO_4 \qquad \log K = 37.82 \qquad \textbf{3.4}$$

*3.3.2.2 Dissolution investigation*

The SS had high buffering capacity. The initial equilibrating solution pH of 0.5, 1.00, and 3.00, when equilibrated with the SS, increased to 6.22, 7.27, and 10.3, respectively (Appendix 3.4). The high acid-neutralising capacity of SS was attributed to the presence of CaO and dissolution of silicates which, as previously mentioned (Appendix 3.6), is accompanied by a rise in pH (Titshall, 2007).

There was a sharp decrease in the concentration of Ca, Fe, and Mn from an equilibrium pH of 6.22 to 7.27 (Figure 3.7). Other elements such as Al, Mg, S, and Si also decreased from an equilibrium pH of 6.22 to 7.27. The concentrations of most elements, with the exception of S, were very low at an equilibrium pH > 10. The release of these elements (Mg, Fe, Ca, Mn, Si, and Al) is most likely to occur due to the dissolution of glaucochroite. Elements such as Fe, Mg, and Al may be present as impurities in glaucochroite. Jonckbloedt (1998) has also reported the release of $Mg^{2+}$ which is replaced by $H^+$ during the dissolution of an olivine.




| Element | Weight (%) |
|---|---|
| Mg | 7.05 |
| Al | 6.41 |
| Si | 24.30 |
| S | 1.86 |
| Ca | 33.86 |
| Ti | 0.44 |
| Mn | 25.07 |
| Fe | 1.04 |
| Total | 100.01 |

**Figure 3.7** (a) A scanning electron microscope image, (b) an EDX trace with a table indicating the composition of smelter slag.

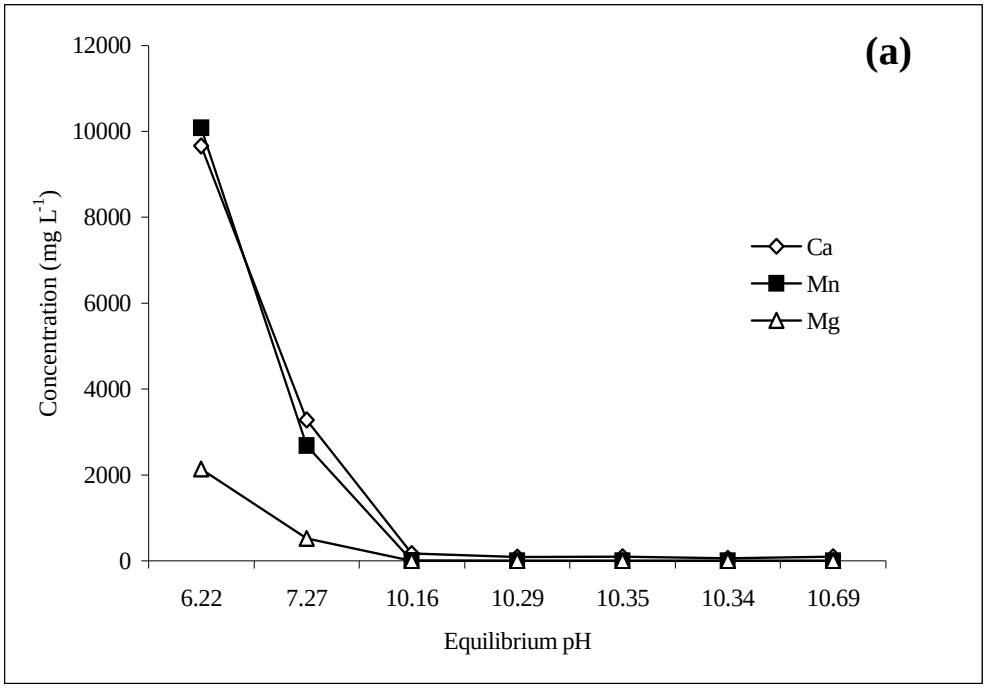
The observed release of elements at different pH is probably reflecting the dissolution of glaucochroite at different pH values. The decrease in the concentration of these elements could be arising from the precipitation of secondary (hydroxide) minerals. These secondary minerals can cause incomplete dissolution of minerals (Appendix 3.6). The low concentration of Si may support the possibility of incomplete dissolution of glaucochroite. Furthermore, the concentrations of Ca and Mn at the equilibrium pH of 6.22 were about 15 and 20 % of total Ca and Mn content, respectively. Sulphur was probably released from gypsum and/or existed exchangeable anion.

These results indicated that the release of Mg, Fe, Ca, Mn, Si, S, and Al from the SS is pH dependent. This has implication for extracting solution whose pH can be buffered to pH above 7 during extraction. Furthermore, consideration must be given to extracting solution that are buffered as the SS has a high acid buffering capacity, which didn't allow the assessment of the release elements at the equilibrium pH below 6.

*3.3.2.3 Adsorption behaviour*

The SS has a high P sorbing/fixing potential (Figure 3.5). The SS P-sorption characteristics at low adsorbate concentration can be described by an L-type curve (Titshall, 2007). There was a sharp increase in P-adsorption of SS at residual P above 22 mg $L^{-1}$ (Figure 3.5) which was attributed to formation of secondary precipitates such as Ca and Mn phosphate (Titshall, 2007). Silicate-rich materials have been reported to reduce P-leaching by forming insoluble phosphate minerals (Kanamugire, 2007). These results indicate that the SS has the potential to minimise the leaching of anionic species of group 4 (McBride, 1994) such as P, Se, As, and possibly V.

The SS adsorption characteristics indicate high affinity of the adsorbent for Zn, Cu, Ni, and Pb (Figure 3.9). The adsorption curve for Cu and Pb tended towards an H-type curve while Zn and Ni were sorbed to a lower extent compared to Pb and Cu and their sorption characteristics can be described by an L-type curve (Figure 3.9) (McBride, 1994).



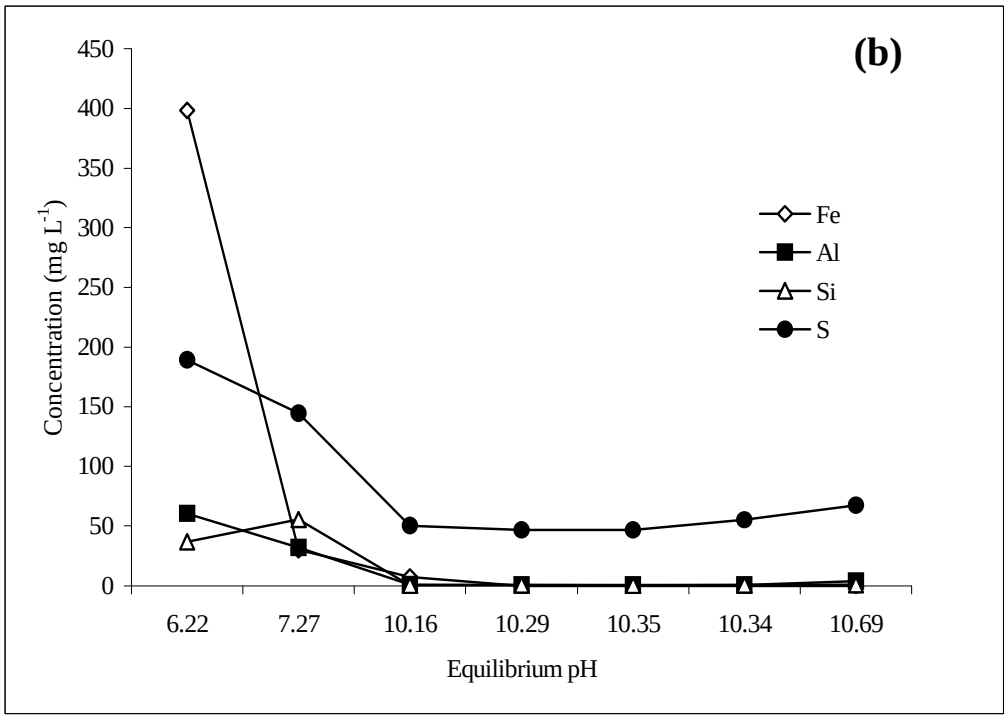




**Figure 3.8** Concentrations of (a) Ca, Mn, and Mg and (b) Fe, Al, Si, and S in equilibration solutions of smelter slag after being treated with solutions of known pH (BHP-Billiton report, 2005).

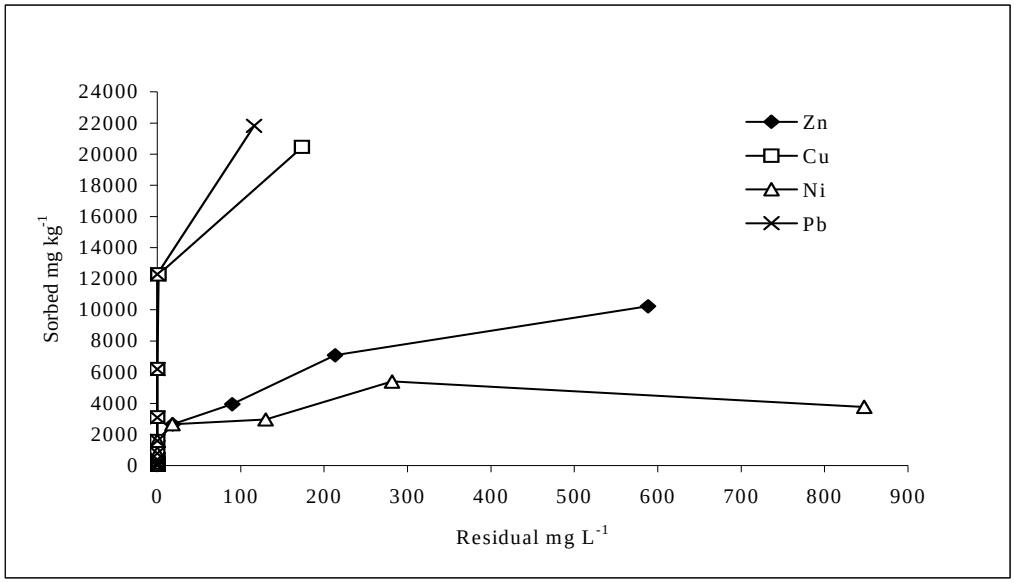



**Figure 3.9** Zinc, Ni, Pb and Cu sorption isotherm of the smelter slag (BHP-Billiton report, 2005).

The observed retention of elements on the SS could be arising from adsorption of these elements on silicate glaucochroite and precipitation of secondary minerals. Most of these elements, with the exception of Ni, can precipitate out as metal hydroxides or as sulphides. Although the presence of sulphide minerals on the SS was not confirmed, Pareuil *et al*. (2010) has reported the presence the of sulphide minerals in a Mn-rich slag. Furthermore, Pb and Cu which were strongly retained are strongly chalcophilic (McBride, 1994). The precipitation of metal hydroxides is favoured at pH above 6 (McLean and Bledsoe, 1992; McBride, 1994). These sorption properties indicate the potential of the SS to immobilise heavy metals, particularly those which are chalcophilic and those which precipitates as metal hydroxides at pH above 6.

### 3.3.3 The Inanda soil form properties

#### *3.3.3.1 Basic properties and mineralogy*

The Ia soil is an acid soil ($pH_{water}$ 4.30 with an acid saturation of 80 %, Table 3.3) which is predominantly composed of hydroxyl-interlayered vermiculites (HIV), kaolinite, hematite, goethite, quartz, and gibbsite with quartz and gibbsite being dominant minerals (Appendix 3.7). The Fe, Si and Al in the Ia soil occurred in the ratio of approximately 2: 2: 3 (Fe: Si: Al, Figure 3.10b). The Ia soil has high OC (9.60 g $100g^{-1}$)

content, high total N, high extractable P and low EC (Table 3.3). Similarly to the EW, the Ia soil was characterised by microporosity and high surface area (Figure 3.10 a). The dissolution reactions and log $K_{dissolution}$ of kaolinite, hematite, goethite, and gibbsite are presented by equation 3.5 to 3.8, respectively (Lindsay, 1979).

**Table 3.3** Physical and chemical properties of the Inanda (Ia) soil form used in the study (Titshall, 2007)

| **Parameter** | | **Soil form**† |
|---|---|---|
| | | **Ia** |
| pH | $H_2O$ | 4.30 |
| | 1 M KCl | 4.00 |
| Electrical conductivity (mS $m^{-1}$) | | 5.42 |
| Organic carbon (g $100g^{-1}$) | | 9.60 |
| Total N (mg $kg^{-1}$) | | 5121 |
| Extractable base cations‡ ($cmol_c$ $kg^{-1}$) | Ca | 0.85 |
| | Mg | 0.20 |
| | K | 0.17 |
| Exchangeable acidity ($cmol_c$ $kg^{-1}$) ‡ | | 4.71 |
| Sum of cations ($cmol_c$ $kg^{-1}$) ‡ | | 5.92 |
| Acid saturation (%)‡ | | 80.0 |
| Cation exchange capacity ($cmol_c$ $kg^{-1}$) | | 13.0 |
| Extractable metal cations‡ (mg $kg^{-1}$) | Mn | 16.0 |
| | Cu | 4.40 |
| | Zn | 2.00 |
| Extractable P (mg $kg^{-1}$) ‡ | | 20.0 |

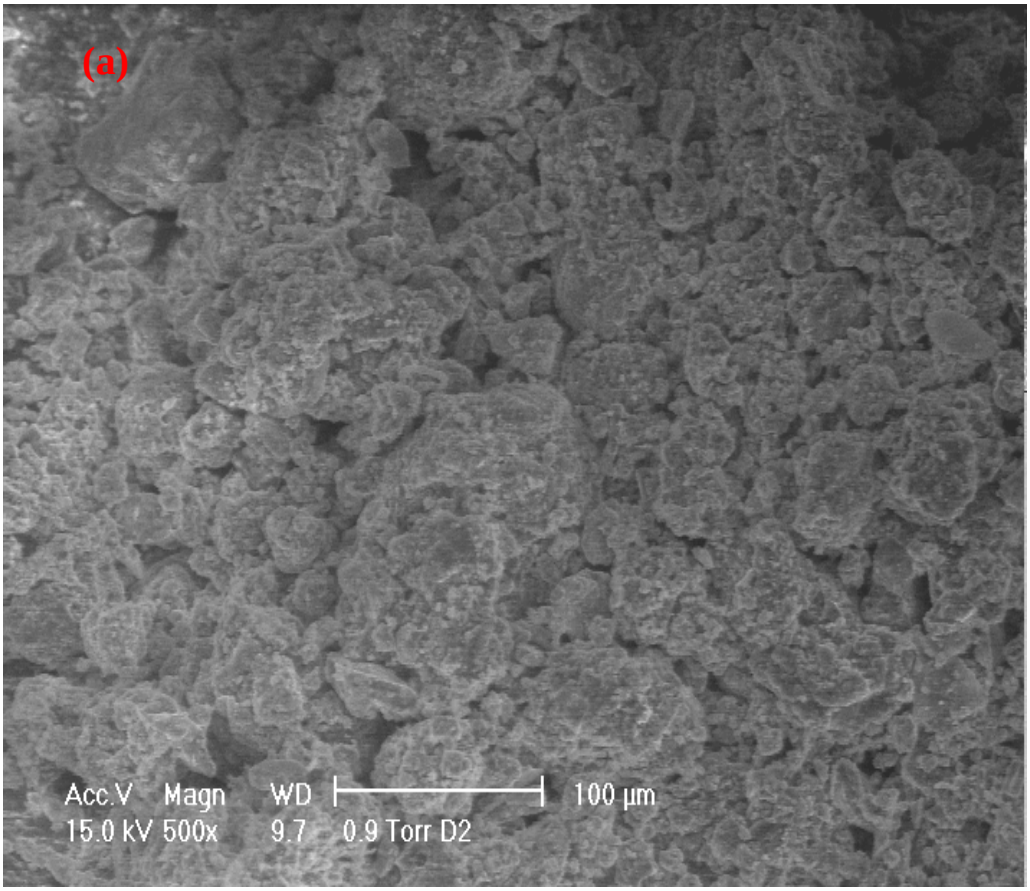
‡ Analysis conducted by the Soil Fertility and Analytical Services Division (KwaZulu-Natal Department of Agriculture, Cedara).

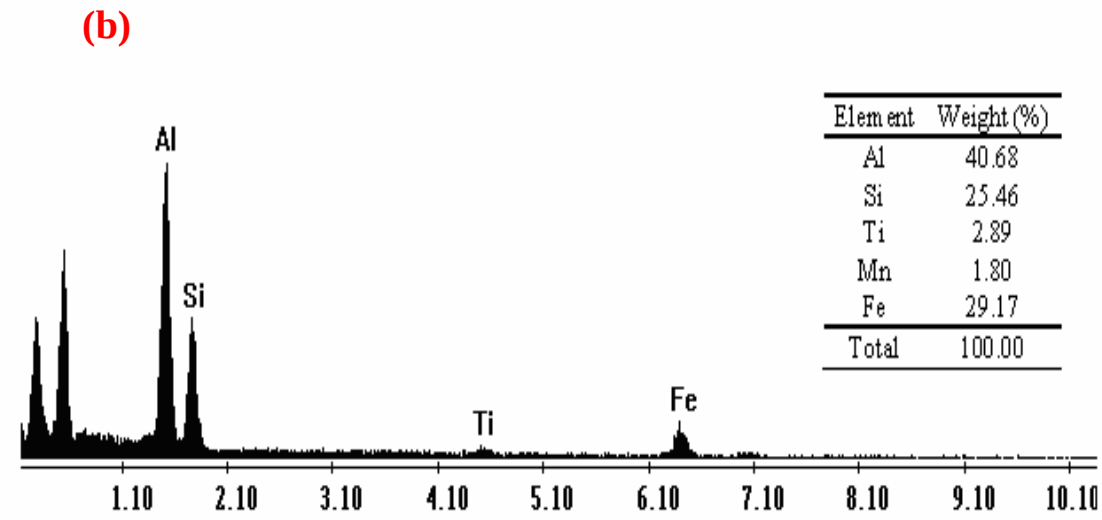
$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightleftharpoons 2Al^{3+} + 2H_4SiO_4 + H_2O \qquad \log K = 5.45 \quad \textbf{3.5}$$

$$\tfrac{1}{2}Fe_2O_3 + 3H^+ \rightleftharpoons Fe^{3+} + 1.5H_2O \qquad \log K = 0.09 \quad \textbf{3.6}$$

$$FeOOH + 3H^+ \rightleftharpoons Fe^{3+} + 2H_20 \qquad \log K = -0.02 \quad \textbf{3.7}$$

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_20 \qquad \log K = 8.04 \quad \textbf{3.8}$$




| Element | Weight (%) |
|---|---|
| Al | 40.68 |
| Si | 25.46 |
| Ti | 2.89 |
| Mn | 1.80 |
| Fe | 29.17 |
| Total | 100.00 |

**Figure 3.10** (a) A scanning electron microscope image, (b) an EDX trace with a table indicating the composition of Inanda soil.

The minerals identified in the Ia soil are characteristically found in highly weathered soils. These minerals, as indicated in equations 3.5 to 3.8, have low solubility in aqueous solution. The Ia soil, because of it mineralogy and organic carbon content, is expected to immobilise heavy metals and also cause the readsoprtion of elements during extractions (Appendix 3.8).

### 3.4 Concluding Remarks

The characterisation of wastes and soils provides information and understanding on the behaviour of materials which has implications for chemical extraction methods and land application of wastes. Chemical extraction methods seem to be affected by the pH, EC, surface characteristics, mineralogy, adsorption properties, and pH buffering capacity of the material under investigation.

The EW was characterised by a near neutral pH, high EC, microporosity and high surface area. It also had a moderate acid and high alkaline buffering capacity. The mineralogical component of the EW was dominated by jacobsite and magnetite. The high EC of the EW is suspected to cause saturation of the extracting solution. The minerals (jacobsite and magnetite) of the EW are stable and might not be completely dissolved by some reagents (such as oxalic acid, hydroxlyammonium chloride, ascorbic acid, and EDTA) used in chemical extraction methods. These two aspects may results in underestimation of the release of elements during extraction. Furthermore, the EW had high sorption capacity which might cause readsorption of released elements during extraction. Nevertheless, the EW is expected to partially dissolve at low pH, in the presence of organic acids, and under both reducing and oxidising conditions. The effect of both reducing and oxidising conditions on the release of elements from the EW will be investigated using the BCR sequential extraction (Chapter 5). The dissolution studies indicated that the partial dissolution of the EW is most likely to occur at final extraction pH below 6. This dissolution would release elements bound on the minerals of the EW and whose release, with the exception of Mg and S, is pH dependent.

The SS has alkaline pH (9.73), low EC, low surface area, high acid buffering capacity, and high P and heavy metals retention capacity. The high retention capacity of the SS

was attributed to formation of secondary precipitates. The mineralogical component of the SS was mainly glaucochroite which is an olivine. Although glaucochroite is highly soluble at low pH and in the presence of organic acids, the low surface area is expected to result in slow dissolution rate. In addition, the dissolution of glaucochroite causes a rise in pH which results in precipitation of secondary minerals. These secondary minerals results in slow dissolution rates and incomplete dissolution of minerals. However, the use of organic acids and chelating agents can complex released elements which will increase the dissolution rates and inhibit the formation of secondary precipitates. The dissolution investigation also indicated that the release of elements from the SS was pH dependent and occurred at the equilibration pH below 10.

The Ia soil was a highly weathered acid soil and was composed predominantly of kaolinite, HIV, quartz, goethite, hematite, and gibbsite. Since Ia soil was highly weathered, it had low concentration of base cations, low pH, and a high organic carbon content. The mineralogical components of the Ia soil and its high organic carbon content suggests that the Ia soil will have a high affinity for heavy metals. Consequently, the Ia soil is expected to contribute to the readsorption of elements released into soil solution.

The use of the SS and EW on the Ia soil based on the above results may have ameliorative effect by reducing the acid saturation of the Ia soil. However, high organic carbon content of Ia soil may results in increased solubility and mobility of elements from these materials. High sorption capacity of the Ia soil, SS, and EW may result in adsorption of released elements before they migrate to groundwater. The adsorption of these released elements may result in redistribution of elements amongst different solid phases. The assessment of redistribution of elements in the SS or EW amended Ia soil would be investigated (Chapter 6). The redistribution of elements may also occur during extraction. Although this is not directly investigated in this study, Chapter 7 and Chapter 8 indirectly deal with this topic.

# CHAPTER 4

# THE EFFECT OF EXTRACTION TIME ON THE SOLUBILITY OF ELEMENTS USING CARBONIC ACID

## 4.1 Introduction

The equilibration or extraction time is important in the chemical extraction of soils and wastes (Ross, 1994). This is because short extraction times may result in incomplete release of elements and long extraction times would result in precipitation of new mineral phases or adsorption of released elements. Incomplete release of elements may underestimate the concentration of elements in the targeted fraction. Precipitation of new mineral phases or adsorption of released elements which will underestimate the concentration of elements from the targeted fraction may also occur. Furthermore, the precipitation of new mineral phases or adsorption of released elements due to saturation of the solution is not likely to occur in field conditions as a fresh solution is supplied.

Another aspect to consider with respect to extraction time is that although chemical extractions are performed in few hours or days, they simulate a long term (days to years) release of elements for plant uptake or to the environment. For instance, exchange reactions are known to be rapid and thus the estimation of the exchangeable cations can be accomplished in an hour or two hours. Whereas, the dissolution of mineral is slow and long extraction times are often used when simulating dissolution reactions.

The assessment of equilibration time is done by monitoring the changes in the concentration of an element or elements with increasing extraction time. If the concentration of the element does not change with increasing extraction time then it is assumed that ‘equilibrium’ had been reached. The extraction time at which the equilibrium concentration is obtained will then be regarded as the ‘standard’ extraction time. Several authors have also regarded the curve plateau as point where equilibrium is reached (Tessier *et al.*, 1979; Maiz *et al*., 1997; Jong and Parry, 2005; Gosh *et al.*, 2006;

Manouchehri *et al.*, 2006; Vann *et al.*, 2006). The equilibration time is expected to be short for desorption of exchangeable elements and longer for the dissolution of minerals.

The equilibration time for the dissolution of minerals has been studied by various authors (Tessier *et al.*, 1979; Bermond, 2001). Tessier *et al.* (1979) assessed the equilibration time for the dissolution of the carbonates and Fe-Mn oxides. Six different times were used to assess the dissolution of carbonates. The concentration of Ca increased with increasing extraction time and then flattened around five hours. In the case of Fe-Mn oxides seven different times were used to assess their dissolution. The concentration curve of Fe released from Fe-Mn oxides reached plateau after six hours. Consequently, an extraction time of five hours was selected for the dissolution of carbonates and six hours for the dissolution of Fe-Mn oxides.

The aim of this chapter was to assess if the carbonic acid extraction recommended in DWAF guidelines (DWAF, 2005b) allow for 'equilibrium' to be reached. Carbonic acid is expected to extract readily mobile elements. Carbonic acid has also been reported to dissolve minerals but there are contradictions in the literature on this matter. Berg and Banwart (2000) reported that carbonic acid, like organic acids, promote mineral dissolution. On contrary, Golubev *et al.* (2005) reported that carbonic acid has no effect on mineral dissolution. These inconsistencies were attributed to the differences in mineral structures (Golubev *et al.*, 2005). However, pH seems to be the principal control that can explain most of these inconsistencies.

Carbonic acid dissociates to either bicarbonate ($HCO_3^-$) or carbonate ($CO_3^{2-}$) ions depending on the pH. Carbonic acid starts dissociating at pH above 4.5 (Bohn *et al.*, 1979). Bicarbonate becomes a dominant species at the pH range of 6.4 to 10.3 whereas carbonate ion is dominant at pH above 10.3 (Bohn *et al.*, 1979; Greenwood and Earnshaw, 1984). Consequently the dissolution of minerals at the pH below 4.5 is proton promoted with no effect from carbonic acid (Berg and Banwart, 2000). Similarly, the dissolution of minerals at pH range of 4.5 to 8 is promoted by both protons and bicarbonate. In the pH range of 8 to 12 the mineral dissolution is controlled

by bicarbonate and carbonate ions. Finally, if the pH is above 12 then the dissolution of minerals is controlled by carbonate ion.

## 4.2 Materials and methods

The changes in the concentration of elements as a function of extraction time were investigated using acid rain test (carbonic acid) on the electro-winning waste (EW), smelter slag (SS), and the Inanda (Ia) soil. In the method outlined (DWAF, 2005b) 100 g of material is extracted with 2 L of carbonic acid for 20 hours. In this investigation a mass of 1 g (< 2 mm) was extracted with 20 ml of carbonic acid. The extraction times investigated here were 16, 20, 30 and 50 hours. The extraction time of 16 hours was chosen to represent extraction time shorter than 20 hours, which is the recommended time. The extraction times of 30 and 50 hours were chosen to represent higher extraction times.

The extractions were performed at room temperature using an end-over-end shaker (at 27 r.p.m). The extracts were separated from the solids by centrifuging at 3000 r.p.m for 20 min and filtered. All the extractions were carried out in triplicate. The filtered extracts were stored at 4 ºC in polyethylene vials for later analysis. The pH of the extracts was measured using Radiometer PHM210 standard pH meter. The concentrations of Al, Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb, S, Si, and Zn in the extracts were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, VARIAN ICP 720-ES). The lower limits of detection for the ICP-OES are presented in Appendix 4.1.

## 4.3 Results and discussion

### 4.3.1 The electro-winning waste

The concentration of Al and Zn did not change appreciably with increasing extraction time (Figure 4.1 a) suggesting that the ‘equilibrium’ was reached before 16 hours for Al and Zn. The concentration of Ca decreased with increasing extraction time (Figure 4.1 b) and the retention of Ca slowed down after 20 hours. The decreasing concentration of Ca with increasing extraction time indicated the presence of Ca removing mechanisms during extraction. These mechanisms could be readsorption of released element or

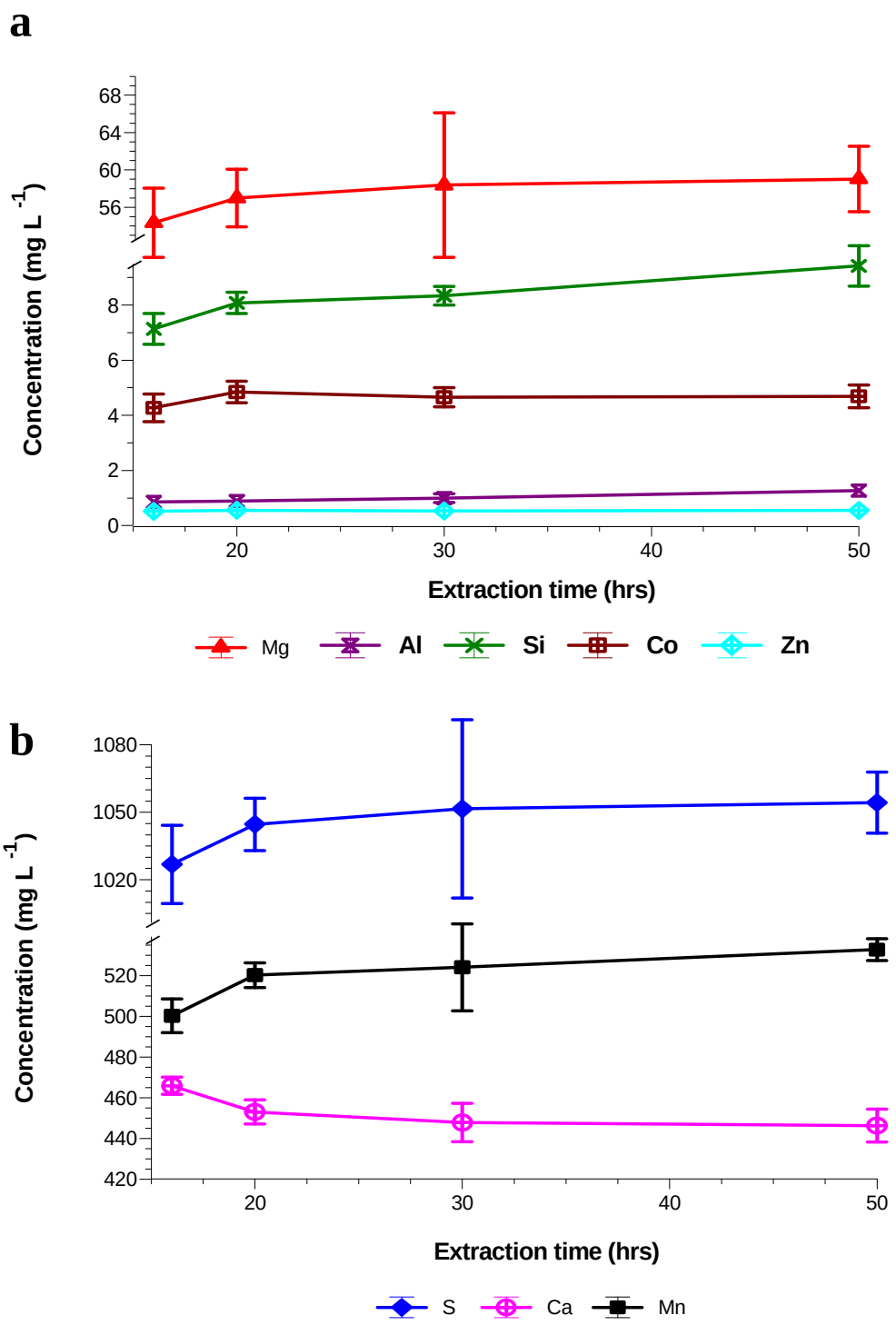



**Figure 4.1** The changes in concentration of (a) Mg, Al, Si, Co, and Zn and (b) S, Ca, and Mn for the electro-winning waste (EW) extracted using carbonic acid for 16, 20, 30, and 50 hours.

precipitation of new solid phases. The final extraction pH for the EW (Appendix 4.2) was below 7 and would not support formation of carbonates. The concentration of S which did not change significantly with increasing extraction time questions the formation of $CaSO_4$ as the Ca removing mechanism. However, the saturation indexes suggested that the extracting solution was supersaturated with respect to gypsum and insoluble $CaSO_4$. Hence the formation of $CaSO_4$ is a possibility.

The other possible mechanism is the readsorption of Ca on exchange sites. In that case, the slowing down of Ca retention after 20 hours may be due to saturation of sorption sites. This mechanism was also proposed by Bermond (2001) who found that Pb concentration began to decrease at the extraction time less than 100 minutes. The decrease of Pb with increasing extraction time was attributed to the readsorption of Pb. However, these mechanisms (precipitation and readsorption) need further investigation. Their effect on elements such as Fe, Cu, Ni, and Pb (which were below detection) needs to be evaluated as it is possible that these elements were also readsorbed or formed secondary precipitates.

The concentration of Co, Mg, Si, S, and Mn extracted from the EW increased with increasing extraction time (Figure 4.1) and the release of Co, Mn, and S slowed after 20 hours indicating that the reaction was nearing completion. The continued increase of Mg and Si after 20 hours could be due to mineral dissolution. This suggests that the release of elements before 20 hours was probably not a result of mineral dissolution. The extraction time less than 20 hours is most likely to release exchangeable and specifically adsorbed elements or cause dissolution of amorphous salts such as gypsum and barite. Beckett (1989) has also indicated that specifically adsorbed elements are released more slowly than exchangeable cations. If the release of elements continues after 20 hours, it is most likely reflecting the release of elements due to mineral dissolution.

These results indicate that 20 hours is adequate to release readily mobile elements though other elements such as Ca (and probably Fe, Cu, Ni, and Pb) might be retained.

Dissolution of minerals may occur at times above 20 hours and might start before the release of readily elements is complete.

4.3.2 The smelter slag

The concentration of Mg, S, and Si did not change appreciably with increasing extraction time in the SS (Figure 4.2) suggesting that the 'equilibrium' was reached before 16 hours for these elements. Conversely, 'equilibrium' was not reached for Ca and Mn. The concentration of Mn decreased from 16 to 20 hours and then increased afterwards which might imply that the release of exchangeable Mn occurred within the first 20 hours and was followed by mineral dissolution which also released Mn. The concentration of Ca in extracting solution increased up to 20 hours and then decreased up to 30 hours which was followed by a subsequent increase. The increasing concentration of Ca before 20 hours represents the release of the exchangeable Ca which was then retained either through precipitation of secondary minerals or readsorption. After 30 hours, the release of Ca through mineral dissolution became dominant.

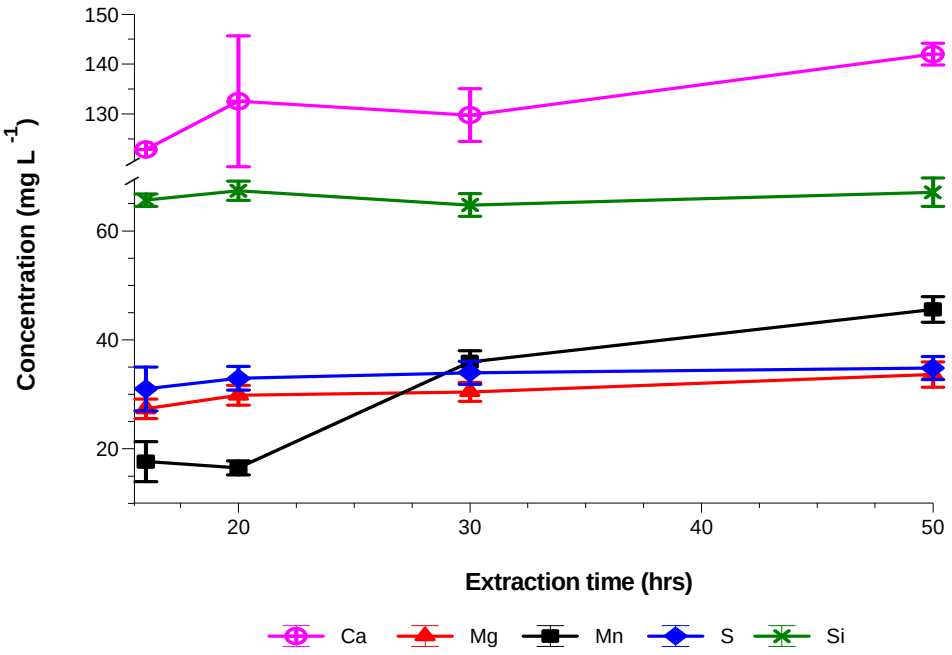



**Figure 4.2** The changes in concentration of Ca, Mg, Mn, S, and Si for the smelter slag (SS) extracted using carbonic acid for 16, 20, 30, and 50 hours.

These results indicate that the release of Ca and Mn using carbonic occurs in two stages which are the release of readily mobile fraction of these elements and through mineral dissolution. Readsorption of released elements or precipitation of secondary minerals may occur between these stages. The dissolution of glaucochroite by carbonic acid should release Ca, Mn, and Si. However, the concentration of Si did not increase with increasing extraction time probably because Si can form polymers and precipitate out as a gel if present in high concentration in solution (Appendix 3.6). Furthermore, the equilibration time for Ca and Mn was not established because of the slow release of these elements arising from mineral dissolution.

4.3.3 The Inanda soil form

The concentration of S did not change appreciably with increasing extraction time suggesting that the 'equilibrium' was reached before 16 hours for S. The concentration of Al, Fe, and Si increased with increasing extraction time (Figure 4.3) and the equilibration time could not be established. The increasing concentration of Al, Fe, and

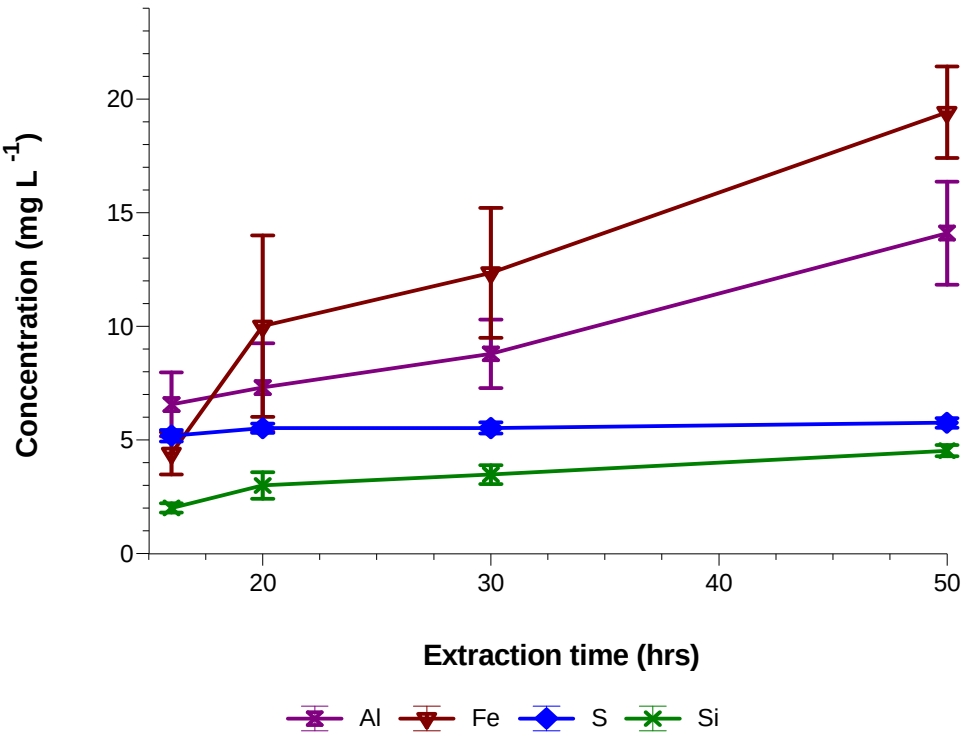



**Figure 4.3** The changes in concentration of Al, Fe, S, and Si for the Inanda (Ia) soil extracted using carbonic acid for 16, 20, 30, and 50 hours.

Si with increasing extraction time, similarly to the SS, might represent dissolution of the soil minerals. Iron would be released from the dissolution of Fe oxides whereas Al would be released from the dissolution of kaolinite and gibbsite. The dissolution of kaolinite would also release Si. Aluminium could also be released from organic matter. However, there was no clear separation between the release of readily mobile elements and those released through mineral dissolution. This was probably due to short equilibration time (less than 16 hours) needed for the release of readily mobile elements or because the release of elements due to mineral dissolution occurred before the release of readily mobile was completed.

Carbonic acid has been reported to dissolve both iron oxides and silicate minerals (Bruno *et al.*, 1992; Berg and Banwart, 2000). The dissolution of kaolinite, iron oxide, and gibbsite consumes protons (equation 3.8 to equation 3.11). This was evident as the final extraction pH was higher than initial pH of both the Ia soil and carbonic acid (Appendix 4.2). Although the effect of pH on the dissolution of these minerals in the presence of carbonic acid was not investigated, these results indicated that the pH increases during the extraction and thus protons are removed by some mechanisms.

## 4.4 Conclusions

The results from this investigation indicated that different fractions of elements are released by carbonic acid from the studied material which made it difficult to establish equilibration time for some elements. The use of equilibration time of 20 hours to assess the release of Mg, Al, Zn, Si, Co, Zn, S, Ca, and Mn in the EW; Mg, S, and Si in the SS; and S in the Ia soil was adequate. These elements were probably exchangeable or specifically adsorbed. However, 20 hours may result in retention of some elements such as Ca in the materials with high sorption capacity like the EW. On contrary, equilibrium was not attained for elements such as Ca and Mn in the SS and Al, Fe, and Si in Ia soil which were most likely released as a result of mineral dissolution.

The release of elements using carbonic acid was found to occur in sequence where the readily mobile fractions are released first followed by mineral dissolution. In some instances the release of elements due to mineral dissolution begins when release of the

readily mobile fraction is not yet complete. This makes it difficult to establish equilibration time for elements which are released from both fractions. Further investigation is required to investigate the effect of pH on the release of elements using carbonic acid, particularly on mineral dissolution. This might assist in separating the release of elements from the readily mobile fraction and those from mineral dissolution.

# CHAPTER 5

# FRACTIONATION OF ELEMENTS IN THE ELECTRO-WINNING WASTE, SMELTER SLAG, AND INANDA SOIL FORM

## 5.1 Introduction

Changes in soil solution chemistry affect the availability of elements. A decrease in pH will release elements bound to carbonates or other acid-soluble material. A shift towards reducing conditions will dissolve Fe-Mn oxides and release elements bound to these oxides. The availability of the released elements may, however, be limited by the precipitation of metal sulphides, which occurs when sulphate are reduced to sulphides (McBride, 1994). These sulphides may dissolve under oxidising conditions which will cause the release metals and possibly sulphuric acid. Furthermore, oxidising conditions can dissolve organic matter causing the release of elements bound to this phase.

Sequential extraction procedures assist in estimating the release of elements with changes in solution chemistry. For instance in the BCR sequential extraction, the release of elements bound to carbonates, Fe-Mn oxides, and organic matter and sulphides is estimated using acetic acid (HOAc), hydroxylammonium chloride (HAC), and hydrogen peroxide ($H_2O_2$), respectively.

The aim of this chapter was to assess the distribution of elements amongst different solid phases of the EW, the SS, and the Ia soil. This distribution was assessed using the BCR sequential extraction and is related to the release of elements with changes in solution chemistry.

## 5.2 Materials and methods

The fractionation of elements was investigated using the BCR three – stage sequential extraction (Quevauviller *et al.*, 1994) with the addition of the final step (residual fraction) aimed at extracting the silicate bound elements (modified from Chen and Ma, 2001) (Table 5.1). The sequential extraction involved the extraction of 0.5 g of a material in a 50 mL polyethylene centrifuge tube with 0.11 M HOAc, followed by

HAC, and then digested with $H_2O_2$ and extracted with 1 M ammonium acetate. The final step involved the digestion with aqua regia. Although aqua regia did not dissolve all the material most of Fe and Mn were removed from the EW (Appendix 5.1). Between each step of the sequential extraction, the sample was rinsed by extracting with 10 mL of distilled water for 15 min and the supernatant liquid was discarded as outlined in the method of Quevauviller *et al.* (1994). The extractions were conducted in triplicates using analytical grade reagents with the exception of $H_2O_2$ which was chemically pure grade. The concentrations of Al, Ca, Co, Cu, Fe, Mg, Mn, Ni, Pb, S, and Zn in the extracts were measured as described in Section 4.2.

**Table 5.1** The different fractions of the sequential extraction with corresponding extractants and volume of extractants, reagents pH, extraction time and temperature. The pH was adjusted using concentrated nitric acid

| **Fractions** | **Reagents and volumes** | **Reagent pH** | **Extraction time** | **Temperature** |
|---|---|---|---|---|
| **Acid-soluble** | 0.11 M $HOAc^{+}$ (20 mL) | nd | 16 hrs | (25 ºC) |
| **Reducible** | 0.1 M $HAC^{++}$ (20 mL) | 2 | 16hrs | (25 ºC) |
| **Oxidisable** | 30% $H_2O_2{}^{+++}$ (5 mL) | nd | 1 hr | 25 ºC |
| | 30% $H_2O_2{}^{+++}$ (5 mL) | nd | 1 hr | 85 ºC |
| | 1 M $NH_4OAc^{++++}$ (35 mL) | 2 | 16hrs | 25 ºC |
| **Residual** | Aqua regia (12 mL) | nd | 16 hrs | 25 ºC |
| | | | 3 hrs | 110 ºC |

| | |
|---|---|
| *nd | not determined |
| $^{+}$HOAc | acetic acid |
| $^{++}$HAC | hydroxylammonium chloride |
| $^{+++}H_2O_2$ | hydrogen peroxide |
| $^{++++}NH_4OAc$ | ammonium acetate |

A separate set of samples was extracted but their solid residues were retained after each extraction to analyse on the XRD (Philips PW1050) and electron microscope (ESEM, Philips XL 30).

## 5.3 Results and discussion

### 5.3.1 The electro-winning waste

The fractionation of elements was investigated using the BCR sequential extraction. The acid-soluble (AS) fraction which includes water soluble and exchangeable elements accounted for a high proportions (> 65%) of extractable Ca, Mg, S, Ni, and Co in the EW (Figure5.1). The release of Ca, Mg, and S is most likely from the dissolution of soluble salts as high concentration of these elements existed as soluble salts. Cobalt and Ni are amongst the most mobile elements of exchangeable heavy metals (Group 2; McBride, 1994) and most likely released through cation exchange. The remainder (< 35%) of Ca, Mg, S, Ni, and Co were in reducible (RF), oxidisable (OX) and residual (RES) fraction. The release of these elements in these fractions could have occurred because they were bound on jacobsite and magnetite. The other possibility is that they were not completely dissolved by acetic acid.

The extractable Cu and Zn had about 35 % in AS and 35 % in RES fractions. The remaining proportions of Zn were in the RF and OX fraction and that of Cu was in the OX fraction. Copper and Zn, like Co and Ni, are exchangeable heavy metals but have a lower mobility compared to Co and Ni. Adsorption studies (Section 3.3.1.3) also indicated that these elements are strongly retained on the EW. These two elements are also known to adsorb strongly on colloidal material (McBride, 1994).

Lead was largely in the OX fraction (about 60 %) and about 35 % Pb was in the RES fraction. In soils $H_2O_2$ is used to dissolve organic matter and sulphides. However, the presence of organic matter and sulphides in the EW is less likely. The high proportion of Pb in the OX was probably released PbS, which could have formed when S is reduced to sulphides, was dissolved. Reducing conditions can results in precipitation of PbS (McBride, 1994) which can be solubilised by $H_2O_2$ and release Pb and S.

Aluminium, Fe and Mn were predominantly in the RES (Figure 5.1). The release of Fe from this fraction suggests that magnetite was not completely dissolved by previous reducing and oxidising reagents but was dissolved by aqua regia. The release of Al might be accounted by the substitution of $Fe^{3+}$ by $Al^{3+}$ on magnetite structure (Schwertmann and Murad, 1990). Jacobsite could have been incompletely dissolved by previous reducing and oxidising reagents but was dissolved by aqua regia which will release both Fe and Mn.

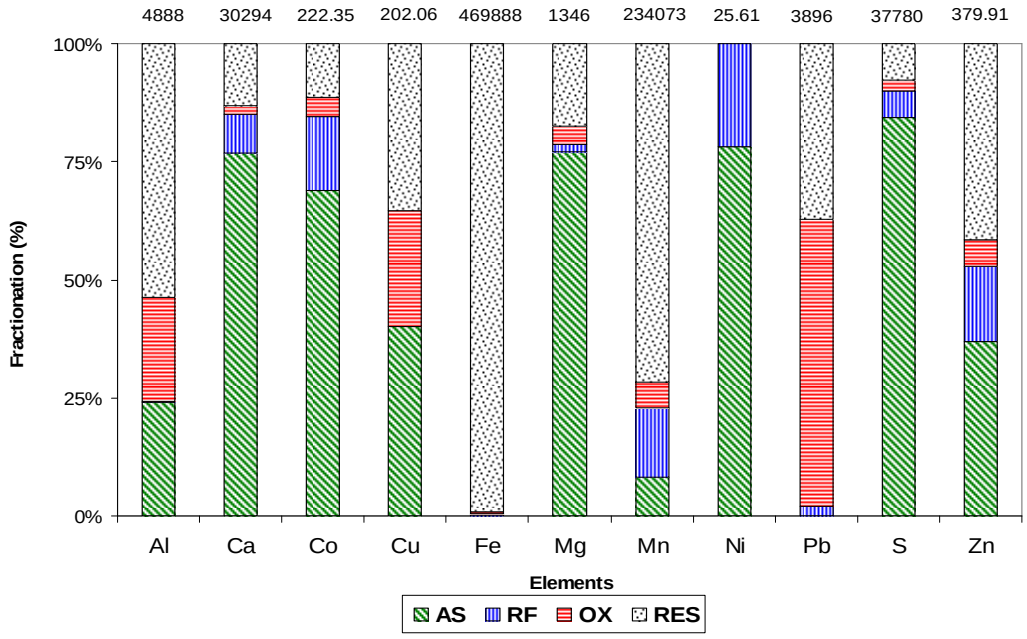



**Figure 5.1** The fractionation of Ca, Fe, Mn, S, Al, Mg, Zn, Cu, Co and Ni amongst the acid soluble (AS), reducible (RF), oxidisable (OX), and residual (RES) fractions for the electro-winning waste. The sum of the concentration (mg $kg^{-1}$) of AS, RF, OF, and RES is presented on top of the bars.

The above results raise the question of whether or not extracting with HOAc followed by HAC and $H_2O_2$ is able to dissolve magnetite and jacobsite which are dominant minerals in the EW. The analysis of the solid residue collected after the $H_2O_2$ extraction using the XRD indicated that both magnetite and jacobsite were still present (Appendix 5.2). Jacobsite and magnetite were dissolved during aqua regia digestion (Appendix 5.2 abd Appendix 5.3).Furthermore, the surface of the EW did not change appreciably after HOAc, HAC, and $H_2O_2$ extraction (Appendix 5.3). Hence it is proposed that HOAc

released elements which were water soluble salts (Ca, Mg, S and small amount Mn) and exchangeable cations (Co, Cu, Ni, and Zn). However, these elements might have not been completely released due to solution saturation or they were readsorbed on jacobsite and magnetite. Extraction with HAC and $H_2O_2$ should release these elements since they might be strongly adsorbed. Furthermore, HAC and $H_2O_2$ may, to a lower extent, dissolve jacobsite without dissolving magnetite. These possibilities questions the BCR sequential extraction's reducing and oxidising reagents ability to dissolve stable minerals such as jacobsite and magnetite.

5.3.2 The smelter slag

The proportions of extractable Al, Ca, Fe, Mg, Mn, and S in the AS were low (< 30 %) for the SS (Figure 5.2). The proportions of these elements in the RF were also low (< 20%). Substantial proportions (> 35%) of Al, Ca, Mg, and Mn were found in the OX for the SS. Similarly, high proportions (> 60 %) of Al, Fe, and S were found in the RES. The RES also accounted for small proportion (< 30%) of Ca, Mn, and Mg.

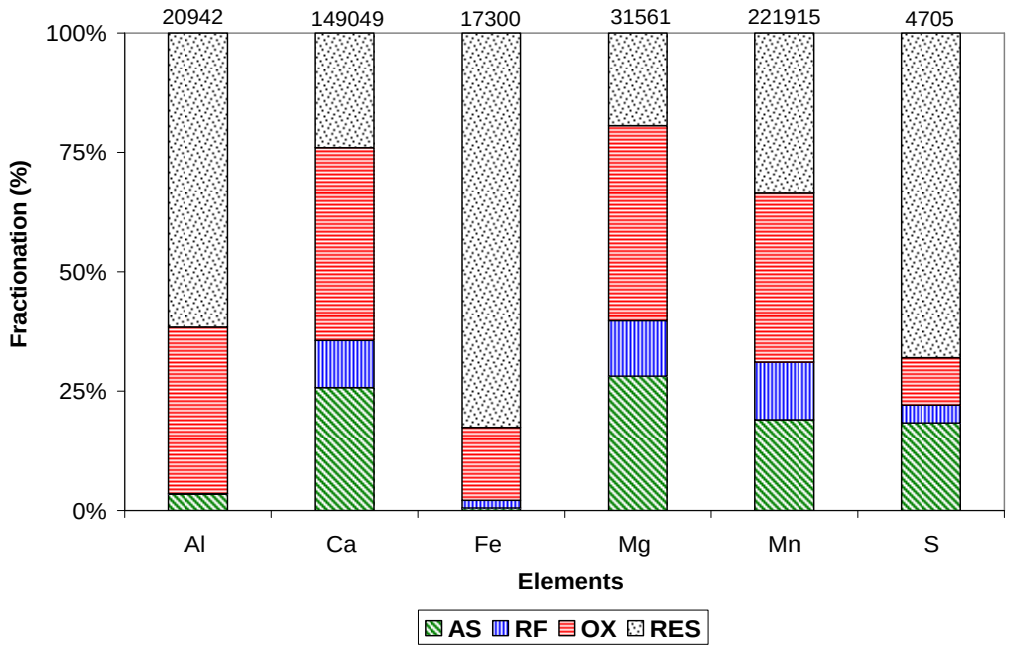



**Figure 5.2** The fractionation of Al, Ca, Fe, Mg, Mn, and S amongst the acid soluble (AS), reducible (RF), oxidisable (OX), and residual (RES) fractions for the smelter slag. The sum of the concentration (mg $kg^{-1}$) of AS, RF, OF, and RES is presented on top of the bars.

The interpretation of the results of the SS obtained from the BCR sequential extraction is difficult. The difficulty arises as the BCR sequential extraction should indicate the release of elements from the SS with changes in solution chemistry but the SS has one predominant mineral (glaucochroite) and small amounts of bustamite and quartz. What could have happened in this case is a progressive dissolution of glaucochroite by the reagents used in the BCR sequential extraction. This progressive dissolution of glaucochroite can be supported by the fact that glaucochroite can be incompletely dissolved due to solution supersaturation and precipitation of secondary minerals (Appendix 3.6). Each reagent used in the BCR sequential extraction gets saturated and the dissolution of glaucochroite stops. Next reagents used allow further dissolution of glaucochroite.

The distribution of Ca and Mn were similar which further supports the progressive dissolution of glaucochroite. The distribution of Mg was also similar to that of Ca and Mn which could have resulted from Mg substituting these elements on glaucochroite. In addition, the analysis of solid residues with the XRD indicated that glaucochroite peaks disappeared after $H_2O_2$ extraction but bustamite's peaks were still present (Appendix 5.4). The analysis of solid residue on electron microscope (Appendix 5.5) shows that HOAc, HAC, and $H_2O_2$ did change (etches were observed) the surface properties of the SS.

Hence, it is proposed that glaucochroite was partially dissolved during HOAc and HAC extraction and the dissolution was accompanied by a rise in pH (Appendix 5.6). The rise in pH would then favour the formation of Al and Fe as secondary (hydroxides) precipitates which would explain the low proportions of these elements in the fractions. However, based on the SEM images formation of secondary precipitates is not conclusive. Nevertheless, the pH changes susggests the formation of secondary precipitaes. As the dissolution of glaucochroite progresses, the SS lost most of its buffering capacity which limited the formation of Fe and Al secondary precipitates. This may result in substantial proportions of Al and Fe in the OX.

High proportions of Al and Fe in the RES could have been released from other secondary minerals such as phosphates and sulphates. Aluminium and Fe sulphates would form when Al and Fe retain S during the dissolution of gypsum. This would explain the high proportion of S in RES. However, high final extraction pH of HOAc (HOAc would dissolve gypsum) is not expected to favour the formation of Al and Fe sulphates. The formation of Al and Fe phosphate would be caused by high phosphorus content in the extracting solution (high P content was measured when the extracting solution was run as a sample on the ICP-OES). These phosphates are stable and their formation is favoured by low pH (Lindsay, 1979). Hence, the high P content of the extracting solution and the low final extraction pH should favour the formation of these phosphates. When these phosphates minerals are dissolved at high temperatures during aqua regia digestion, Al and Fe would be released.

Although the release of elements from the SS using the BCR sequential extraction could be traced and explained, consideration needs to be taken as the results obtained do not reflect the release of elements with changes in solution redox chemistry. However, the results from the BCR sequential extraction may indicate the release of elements from the SS due to continued acidification.

### 5.3.3 The Inanda soil form

The elements in the Ia soil behaved differently to those in the wastes. Firstly, the total extractable elements were lower in the Ia soil than in the wastes with the exception of Al and Ni. Secondly, high proportions (> 85%) of elements, with the exception of Ca, S, and Cu, were found in the RES (Figure 5.3). The RES also accounted for more than 65 % of S and Cu and about 45 % of Ca. About 40 % of Ca was found in the AS with the remaining Ca accounted for by the RF and the OX. The RF also accounted for about 25 % Cu, and less than 5 % of Al, Fe, and S. Similar proportions (<5 %) of Al and Fe were found in the OX. The OX accounted for about 25 % S which was probably present as organic S, particularly since Ia soil has high organic matter content.

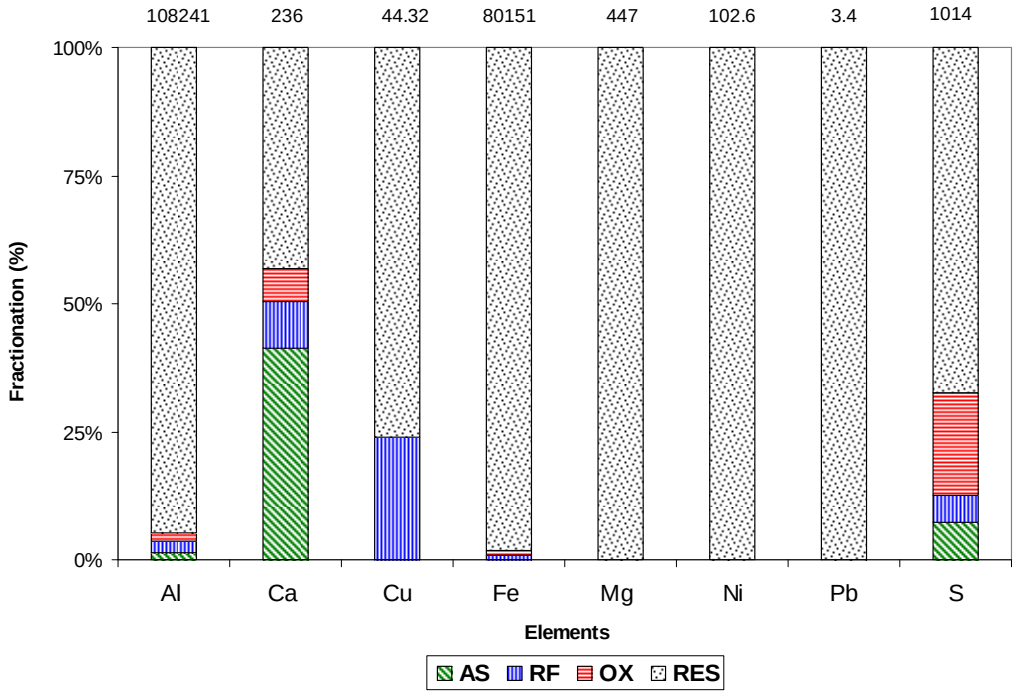



**Figure 5.3** The fractionation of Al, Ca, S, Fe, Mg, Ni, Pb, and Cu, amongst the acid soluble (AS), reducible (RF), oxidisable (OX), and residual (RES) fractions for the Inanda soil form. The sum of the concentration (mg $kg^{-1}$) of AS, RF, OF, and RES is presented on top of the bars.

The Ia soil is highly weathered and has most of extractable elements leached. As a result, most elements are incorporated into crystalline materials during weathering. This would explain high proportions of elements in the RES. Small proportion of Al in AS might have been present as water soluble Al which is known to be a problem in highly weathered acid soils or complexed by soluble organic matter. Similarly, Ca and S are expected to be water soluble. The elements in RF might have been released during the dissolution amorphous Fe oxides. This is because the crystalline minerals were not dissolved by HOAc, HAC, and $H_2O_2$ and the analysis of solid residues using the XRD indicated that HIV, kaolinite, goethite, and hematite were still present after $H_2O_2$ extraction (Appendix 5.7). However, $H_2O_2$ might have dissolved organic matter and released organically bound S. Nevertheless, the results of the BCR sequential extraction indicate that lower concentration of elements will be released from the Ia soil when acidification, reducing and oxidising conditions occurs.

## 5.4 Conclusions

This chapter showed that the release of elements from Ia soil is not similar to those in the EW and the SS. A question was also raised regarding the use of the BCR sequential extraction to estimate the release of elements with changes in solution chemistry. Magnetite and jacobsite from the EW were not substantially dissolved by the HOAc, HAC, and $H_2O_2$ used in the BCR sequential extraction which could have arisen from these reagents being less aggressive. This could have also been caused by dynamic behaviour of jacobsite, which when it dissolves it can form magnetite and manganese dioxide. Furthermore, $H_2O_2$ which is supposed to be an oxidising agent probably operated as a reducing agent. The limitation of the BCR sequential extraction in the SS was that the predominant mineral (glaucochroite) is not dissolved by reducing and oxidising conditions. Glaucochroite is, however, dissolved by continued acidification caused by a successive application of HOAc, HAC, and $H_2O_2$. There is a possibility that secondary minerals such as sulphates and phosphate are formed during the sequential extraction. This formation of secondary minerals reduces the availability of elements such Al and Fe. Further investigation is needed that will assess the effect of using reducing and oxidising reagents which are different to those used in the BCR sequential extraction. This further investigation should also attempt to use higher solution to solid ratio in order to avoid saturation of the extracting solution.

# CHAPTER 6

# THE EFFECT OF INCUBATION TIME ON THE AVAILABILITY OF ELEMENTS FROM WASTE TREATED SOIL

## 6.1 Introduction

The availability of elements may change over time when a waste is applied to soils. These changes are governed by dissolution-precipitation and adsorption-desorption processes. Basta *et al*. (2005) indicated that the degradation of organic matter and dissolution Fe-Mn oxide minerals release elements bound to these solid phase into solution. Organic matter, Fe-Mn oxides, and other solids (such as carbonates) can, through adsorption, immobilise a substantial amount of pollutants. This combined release and readsorption of elements will result in redistribution of elements amongst different solid phases in waste treated soils.

The objective of land application of waste is to utilise the chemical, physical, biological properties of soil to assimilate waste components with minimal effects on soil, water and air quality (Cameron *et al.*, 1997). This implies that the toxic effect of waste and availability of pollutants from the waste are expected to decrease when waste is applied to soil. Sequential extraction procedures (SEP) can give insight into the immobilisation or redistribution of elements in soil. These are said to "*furnish detailed information about the origin, mode of occurrence, biological and physiochemical availability, mobilization, and transport of trace metals*" (Tessier *et al.*, 1979).

The effect of incubation time on the mobility and distribution of elements in waste amended soil was investigated in this study. The changes in the availability of elements were investigated using a water extraction and the BCR sequential extractions. The water extraction represents the most mobile elements and closely resembles soil solution and the BCR sequential extractions will assess the redistribution of elements.

## 6.2 Materials and Methods

### 6.2.1 Incubation experiment

The SS and EW were mixed with the Ia soil at rates of 120 and 20 g $kg^{-1}$ respectively. The equivalent 'field' application rates were 288 Mg $ha^{-1}$ for the SS and 48 Mg $ha^{-1}$ for the EW (assuming a soil bulk density of 1.2 g $cm^{-3}$ and an incorporation depth of 200 mm). The application rate of the SS was chosen as it maintained the pH of Ia soil around 6.5 which minimised nutrient deficiency and that of the EW was chosen to keep the EC at lowest levels (Titshall, 2007). After thorough mixing of soil and wastes, the mixtures were moistened to field capacity by adding distilled water. Field capacity was considered to be the water content of the soil:waste mixture at a matric potential of -30 kPa. The moistened mixtures were remixed and placed in plastics bags and stored in dark plastic buckets at 24ºC. The bags were opened and mixed weekly to prevent anaerobic conditions from developing. The mixtures were then sampled after 7, 28, 56, and 140 days. A separate dry mixture was prepared and considered as time zero (Day 0). These samples are represented as EW 0, EW 7, EW 28, EW 56, and EW 140 for the EW mixture and SS 0, SS 7, SS 28, SS 56, and SS 140 for the SS mixture. After sampling, the mixtures were immediately air-dried and re-milled (to pass through a 2 mm sieve) for analysis. It was assumed that air drying stopped further reactions from occurring.

### 6.2.2 Changes in availability of elements as a function of incubation time

The changes in water extractable elements as a function of incubation time were investigated using the method of Dold (2003). A mass of 0.6 g (of samples from the incubation experiment) was extracted with 30 ml of distilled water for 1 hour at room temperature.

The changes in the distribution of elements over time in the waste amended soil were investigated using the BCR three–stage sequential extraction (Quevauviller *et al.,* 1994) (Section 5.2). The analysis of the extract was carried out as outline in Section 4.2.

## 6.3 Results and Discussion

6.3.1 Changes in the water soluble elements with incubation time

*6.3.1.1 The electro-winning waste*

The concentration of water soluble Ca, Mn and Mg increased with incubation time for the EW treated soil (Figure 6.1) indicating that there were reactions between the Ia soil and the EW that caused the release of these elements. The concentration of water soluble S decreased with incubation time (Figure 6.1) suggesting the removal of S from soil solution. The concentration of water extractable Al did not change appreciable with incubation time.

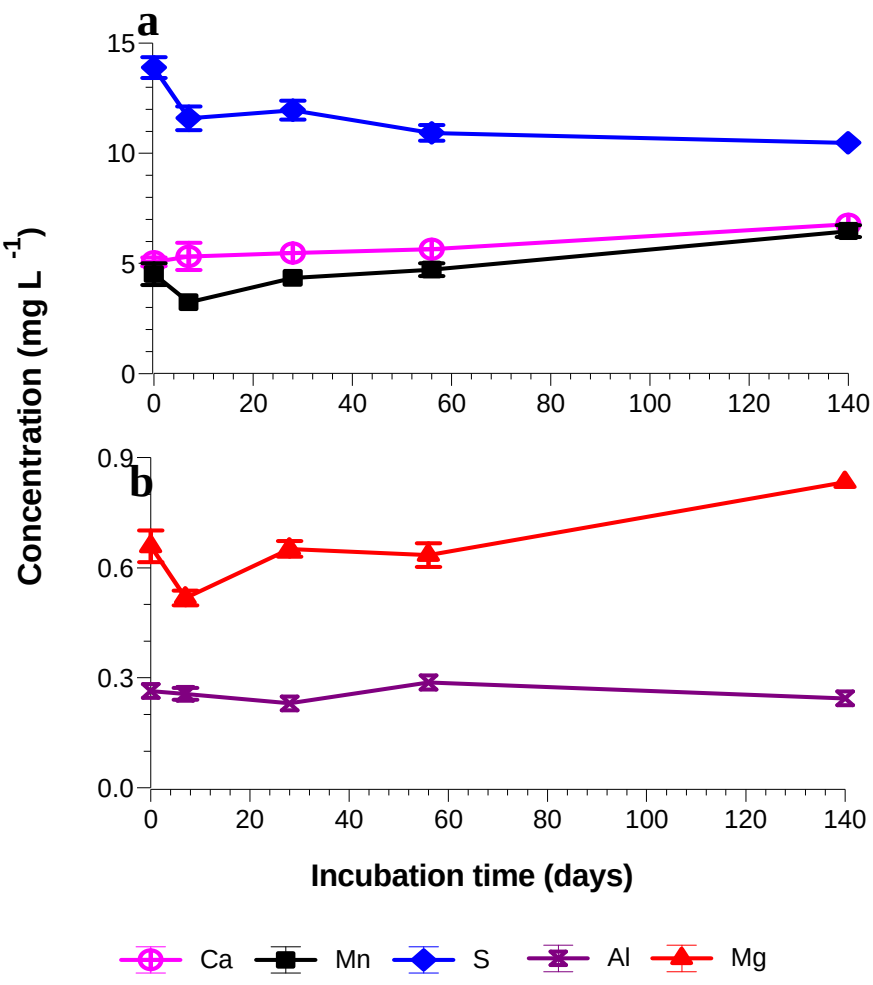



**Figure 6.1** The changes in the concentration of water soluble (a) Ca, Mn, and S, and (b) Al and Mg with incubation time for an electro-winning waste treated soil.

The release of Ca, Mn, and Mg might have been caused by complexation of these elements by organic acids and by increased acidity. The Ia soil contains organic acids which can cause desorption of elements from the surfaces or cause dissolution of solid phases at the low pH of Ia soil. Elements availability is increased and then maintained when organic acids form water soluble metal complexes (Lindsay, 1979; Ross, 1994; Schwab *et al.*, 2008).

The production of organic acids (when organic matter decomposes) will also lower the pH of the soil solution (Titshall, 2007). A decrease in pH can also be caused by nitrification (equation 6.1; Bloom, 2000). The EW has high ammonia content which can be transformed to nitrate and produce acidity. The low pH will enhance the dissolution of minerals. Both low pH and organic ligands have been reported to cause the dissolution of minerals (Stone and Morgan, 1984; Chorover and Sposito, 1995; Drever and Stillings, 1997; Li and Schwartz, 2004).

$$2NH_4^+ + 4O_2 \rightleftharpoons 2NO_3^- + 4H^+ + 2H_2O \qquad \textbf{6.1}$$

This decrease pH with incubation time was assumed to cause the decrease in water soluble S with incubation time. The decrease in pH will results in positively charged surfaces which will increase anion exchange capacity (AEC). The positively charged surfaces will cause adsorption of sulphate-S on mineral surfaces.

*6.3.1.2 The smelter slag*

The concentration of water soluble Al increased from Day 0 to Day 7 and then decreased afterwards (Figure 6.2). The concentration of water soluble Al was below detection by Day 56. The concentration of water soluble Ca, S, Mg, Mn, and Si, on the contrary, increased with incubation time for the SS treated soil (Figure 6.2). Calcium and Mg were below detection on Day 0 appeared in solution by Day 7. Water soluble Mn was also below detection up to Day 28 and by Day 56 it had appeared in solution. The increasing concentration of water soluble Ca, Mn, S, and Si could be arising from the dissolution of glaucochroite and gypsum. The decreasing concentration of water soluble Al might be caused by precipitation of Al hydroxides.

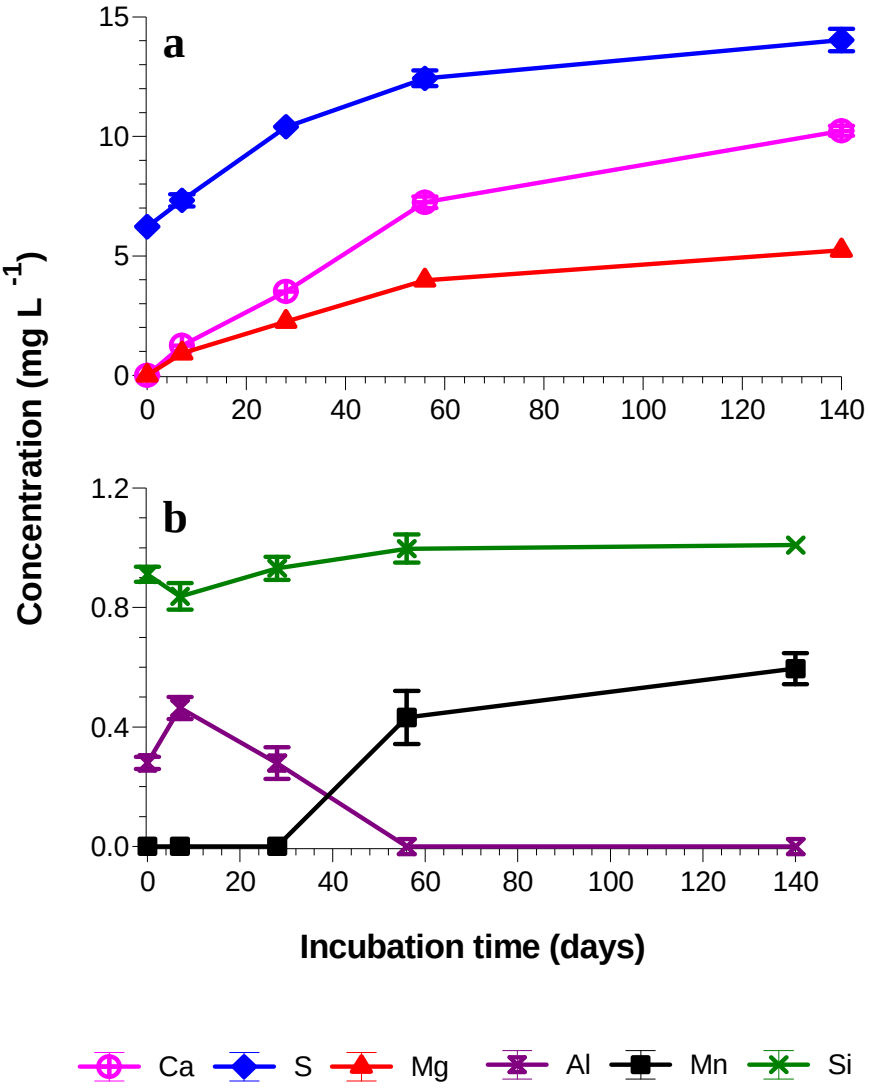



**Figure 6.2** The changes in the concentration of water soluble (a) Ca, S and Mg, and (b) Al, Mg, and Si with incubation time extracted in a smelter slag treated soil. The concentration of zero represents concentration of elements which were below detection.

The dissolution of glaucochroite might have occurred by Day 7 which is supported by decreasing water soluble Al and appearance of Ca and Mg in solution. The dissolution of glaucochroite results in the increase in pH (Appendix 3.6) which will remove Al from solution by forming Al hydroxides minerals. Matichenkov and Bocharnikova (2001) have also postulated that silicate materials can lower Al toxicity by increasing

the pH of the acid soils. The release of Mn might have occurred on Day 7 but the concentration was too low to be detected. Hence as the dissolution of glaucochroite continues the concentration of Mn increased and was detected after Day 28.

The increasing pH is expected to increase the CEC and, hence, the adsorption of cations is expected to increase and their concentration in solution to decrease. However, Al was the only cation whose concentration decreased with increasing pH. It was assumed that organic acids, produced when organic matter decomposes, complexed other cations and inhibited their adsorption.

### 6.3.2 The effect of incubation time on the distribution of elements

#### *6.3.2.1 The electro-winning waste*

The BCR sequential extraction was used to investigate the changes in distribution of elements amongst different mineral phases as function of incubation time in waste amended soil. The distribution of Al, Fe, and Mg did not change appreciably with incubation time in the EW treated soil (Figure 6.3). Calcium and S decrease with incubation time in the AS fraction (Figure 6.3). The decrease of Ca in the AS fraction corresponded to an increase RF, OX, and RES fractions, particularly the RF fraction (Figure 6.3 a). The decrease of S in the AS corresponded to an increase of S in OX and RES (Figure 6.3 d). This decrease of S was not unexpected as water soluble S decreased (Figure 6.1 a) in the EW treated soil.

There are three possibilities that may explain the behaviour of Ca and S but only one of these possibilities includes the retention of both elements by the same mechanism. The first one is that S was released from the acid-soluble materials during acetic acid extraction and was adsorbed on organic matter or formed stable minerals such as barite ($BaSO_4$). The second possibility is that Ca was readsorbed on organic matter and Fe-Mn oxides during acetic acid extraction. This would result in, and might explain the increasing Ca with incubation time in the RF, OX, and RES fractions. The third possibility is that the same mechanism that is removing S is also removing Ca.

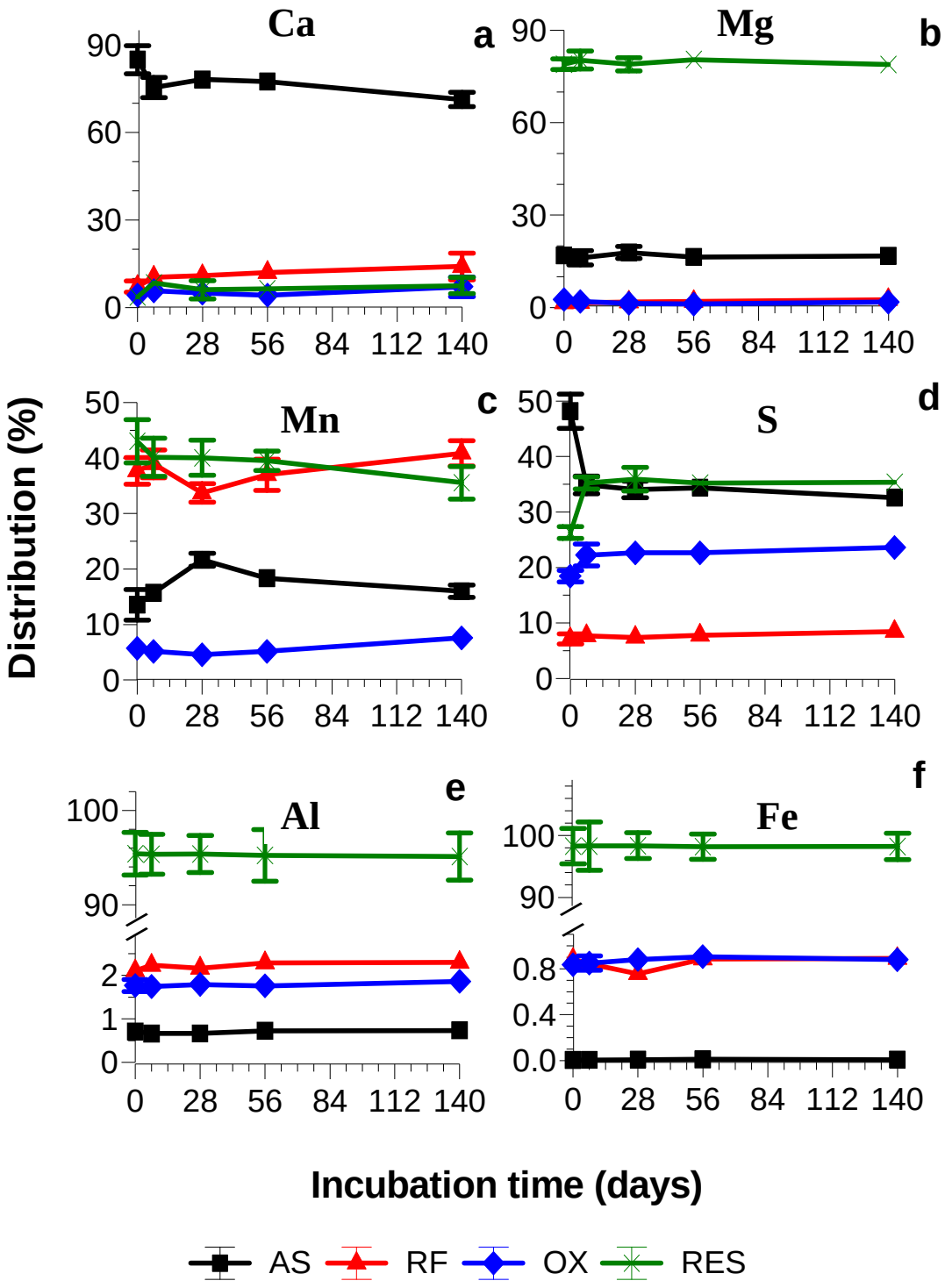



**Figure 6.3** The changes in the distribution of (a) Ca, (b) Mg, (c) Mn, (d) S, (e) Al, and (f) Fe amongst the acid soluble (AS), reducible (RF), oxidisable (OX) and residual (RES) fractions as function of incubation time in electro-winning waste treated soil.

The results of the decreasing Ca in the AS contradicted those of increasing Ca in the water extraction. The decreasing Ca in the AS could be caused by the readsorption of Ca during HOAc extraction. When assessing the effect of extraction time in the extractability of elements, the results indicated that Ca gets readsorbed in the EW during carbonic acid extraction if the extraction time is too long. This was proposed as possibility and although HOAc may behave differently from carbonic acid readsorption during HOAc extraction can occur. The HOAc extraction was performed for 16 hours by which readsorption of Ca is most likely to occur whereas the water extraction is performed for 1 hour which is not long enough to results in readsorption of Ca.

The decreasing Ca with incubation time in the AS fraction questions the readsorption of Ca during acetic acid extraction. Furthermore, decreasing pH in the EW treated soils (Titshall, 2007) and low final extraction pH is not expected to favour the readsorption of Ca. Hence, the decreasing Ca with incubation time in the AS fraction was probably due to the formation of insoluble calcium sulphate (the third possibility) which is favoured by high sulphate concentration and low pH (Lindsay, 1979).

The increasing S (exchanged by acetate ion) in solution and decreasing pH with incubation time were probably the main factors causing the formation of insoluble calcium sulphate. The decreasing pH with incubation time will cause the release of Ca and retention of S as observed in Figure 6.1. When acetic is applied to the EW treated soils it will release exchangeable S as acetate ion has been used to assess the concentration of anions in the exchangeable fraction (Peralta *et al.*, 1996). In this instance sulphate would exchanged by acetate ion. Furthermore, acetic acid extraction will dissolve gypsum and release $Ca^{2+}$ and $SO_4^{2-}$ into solution. High concentration of calcium and sulphur in solution would results in supersaturation of the solution with respect to calcium sulphate which is insoluble (Lindsay, 1979) and the formation of calcium sulphate.

The decreasing Ca with incubation time would then imply that there is an increasing release of S, which react Ca and form more calcium sulphate, with incubation time in the AS fraction. This may indicate that there are other anions whose release increases

with incubation time and are also exchanging sulphates. These anions are probably anions from organic acids which are released as organic matter decomposes with incubation time.

The decreasing Ca with incubation time in the AS fraction is thus a function of both the incubation time and extraction. The increasing Ca in the RF, OX, and RES fractions may be suggesting the dissolution of calcium sulphate by hydroxylammonium chloride, hydrogen peroxide, and aqua regia, particularly hydroxylammonium chloride.

Manganese decreased with incubation time in the RES fraction (Figure 6.3 c). The decrease of Mn in the RES fraction corresponded to an increase in the AS fraction up to 28 Days. After 28 Days there was a decreased of Mn in the AS fraction corresponding to an increase of Mn in the RF fraction. The release of Mn from the crystalline materials such as jacobsite would cause an increase in the AS fraction (which measures water soluble, exchangeable and AS fraction). The released Mn becomes adsorbed on the easily reducible oxides. Hseu (2006) also observed the increase of Zn with incubation time in the RF fraction on soils incubated with biosolids. This increase of Zn in the RF fraction was attributed to the adsorption of Zn released from organic matter on Fe-Mn oxides. Tang *et al*. (2006) and Jalali and Khanlari (2008) have also observed increase of Cd, Cu, Pb, and Zn in RF fraction and attributed this trend to adsorption of elements by Fe-Mn oxides. The oxides Fe-Mn are known to play an important role in the mobility of pollutants in the environment (Neaman *et al.*, 2004a; Silveira *et al.*, 2006). These oxides strongly adsorb heavy metals and can immobilise substantial amount of pollutants (Chao, 1972; Chao and Zhou, 1983; van Herck and Vandecasteele, 2001).

*6.3.2.2 The smelter slag*

The changes in the distribution of elements with incubation time in the SS treated soil were mainly associated with the RES fraction (Figure 6.4). Generally, the concentration of Ca, Mn, Mg, and Al decreased from Day 0 to Day 7 and then increased afterwards in RES fraction on the SS treated soil. The concentration of these elements increased and was equal to initial (Day 0) concentration and did not change with continued incubation. The decreasing concentration of S in the RES fraction corresponded to an increase S in

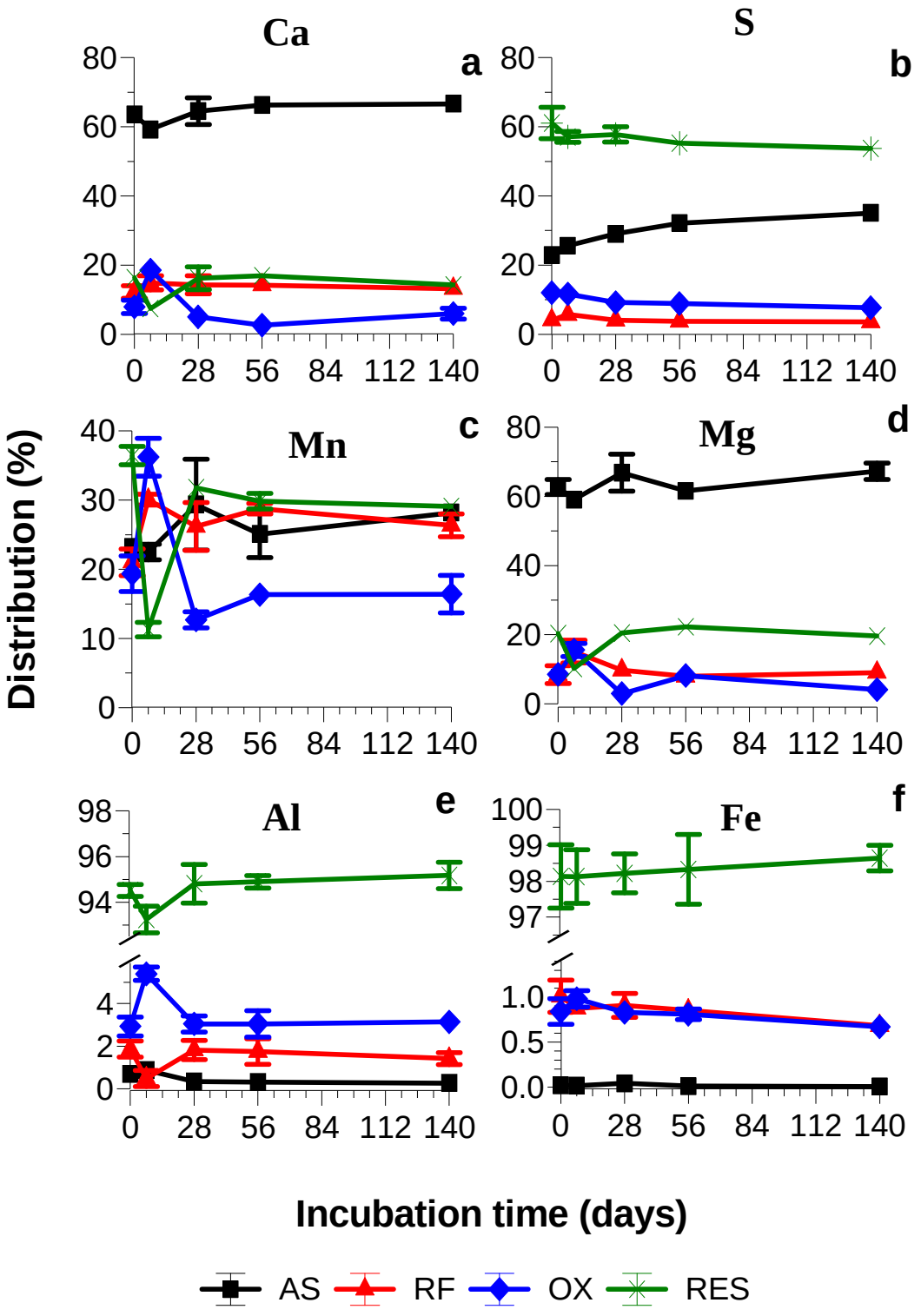



**Figure 6.4** The changes in the distribution of (a) Ca, (b) S, (c) Mn, (d) Mg, (e) Al, and (f) Fe amongst the acid soluble (AS), reducible (RF), oxidisable (OX) and residual (RES) fractions as function of incubation time in smelter slag treated soil.

the AS fraction. The increasing S in the AS is similar to the increasing S in the water extraction with incubation time and may reflect the release of S with increasing pH. As the pH increases with incubation time the AEC will decrease which will results in the release of anions such as sulphates.

The decrease in the concentration of Ca, Mg, and Mn in the RES fraction corresponded mainly with an increase in the RF fraction. This may suggest that easily reducible oxides contributed in the adsorption of Ca, Mg, and Mn. Organic matter may have also contributed in the adsorption of Ca, Mg, and Mn as the concentrations of these elements increases from Day 0 to Day 7 in this fraction and decreases afterwards. The behaviour of Ca, Mg, and Mn may support Tate's (1987) argument (Appendix 3.8).

The changes in the concentration of Al with incubation time in the RES fraction corresponded to the changes in the OX fractions. These results suggest that the Al released from crystalline materials was adsorbed organic matter. When organic matter started dissolving, Al was adsorbed on crystalline silicate (such as kaolinite) and gibbsite.

### 6.4 Conclusions

The changes in the availability of elements with incubation time were investigated using water and the BCR sequential extraction. The water extraction indicated that the solubility of Ca, Mg, and Mn increased with incubation time in the EW treated soil. This might have resulted from the dissolution of minerals due to production of organic acids when organic matter decomposes and low pH caused by nitrification of ammonia in the EW. The low pH of the EW treated soil was also assumed to results in the decreasing S in water extraction as a function of incubation time. The BCR sequential extraction showed that the availability of Ca, Mn, and S decreased with incubation time in the EW treated soil. The reduction in availability of these elements was likely due to the adsorption of these elements on Fe-Mn oxides, organic matter, and crystalline silicate minerals. The contradicting trends between water extraction and the AS fraction were attributed to the formation of insoluble calcium sulphate during HOAc extraction.

The solubility of Ca, S, Mg, Mn, and Si also increased with incubation time in the SS treated soil. In the SS treated soil there was an initial decrease in RES fraction of Ca, Mn, Mg, and Al which increased after Day 7. This was attributed to the adsorption of these elements on organic matter and easily reducible oxides. On overall the elements were associated with least soluble fractions.

# CHAPTER 7

# A COMPARISON BETWEEN THE SEQUENTIAL AND BATCH EXTRACTIONS FOR THE EXCHANGEABLE AND ACID-SOLUBLE ELEMENTS

## 7.1 Introduction

The Community Bureau of Reference (BCR, now known as the Standards, Measurements and Testing Programme) three-step sequential extraction was developed to offer a standardised SEP (Quevauviller *et al.*, 1994). However, the BCR sequential extraction which starts with an acid soluble extraction does not include a separate assessment of water soluble and exchangeable fractions. This offers a compromise between the number of steps employed and in the amount of information obtained (Perez-Cid *et al.*, 1996). As a result, information on the distribution of the mobile phases is not obtained due to a reduction in the number of steps used in this procedure compared to other methods.

Most sequential extraction procedures include a separated measurement of both the water soluble, exchangeable, and the acid-soluble fractions (Tessier *et al*., 1979; Krishnamurti *et al.*, 1995) in their protocol. The availability of elements associated with each of these three fractions is different and their simultaneous assessment as done in the BCR sequential extraction (Quevauviller *et al.*, 1994) is questionable.

Another common practise is a simultaneous measurement of the water soluble and exchangeable elements (Ahnstrom and Parker, 1999; Mbila *et al.*, 2001). The water soluble fraction contains free ions, ions complexed with soluble organic matter, neutral salts and other constituents (Miller *et al.*, 1986; van Herck and Vandecasteele, 2001; Filgueiras *et al.*, 2002). The exchangeable elements, though attached to the soil surfaces, are considered to be readily mobile and easily bioavailable. The elements which are exchangeable are often assessed by the application of neutral salts and are usually closely related to plant uptake (Shuman, 1978). On the other hand, acid soluble

elements are released when solids such as carbonates or other acid soluble components are dissolved at low pH.

The objective of this investigation was to determine whether or not the inclusion of water soluble and exchangeable fractions in the BCR sequential extraction protocol is necessary. This was done by determining water soluble, exchangeable and acid soluble fraction as sequential extractions and comparing the results to single batch extractions using the same three reagents. The postulate was that concentration of elements found in sequential and batch extractions would be comparable. This is based on the fact that the reagents in sequential extractions are applied in order of increasing strength so that fractions of elements extracted later correspond to a lesser mobility (Filgueiras *et al.*, 2002). Hence, reagents used later in sequential extraction, when applied as single batch extraction, are expected to also extract the fraction of elements that would be removed by earlier reagents.

## 7.2 Materials and Methods

Two wastes and one uncontaminated soil (EW, SS and the Ia soil used in Chapter 3) and soil waste mixtures (used in Chapter 6) were used in this investigation. The assessment of the need to include the water soluble and exchangeable fractions in the BCR sequential extraction was carried out by applying reagents in Table 7.1 as both sequential and batch extractions. In brief, 0.6 g of a material was placed in a 50 ml polyethylene centrifuge tube and was extracted with distilled water (Dold, 2003), 1 M ammonium nitrate (Lin *et al.*, 2004) and 0.11 M acetic acid, either sequentially or batchwise. For the sequential extractions reagents were applied in sequence on the same sample and for the batch extractions each reagent was used to extract a separate sample, using the same soil:solution ratios and extraction times as in sequential extractions. The extraction times and volumes of the extracting solution are presented in Table 7.1. Solutions were separated, stored, and analysed for pH and elemental concentration as described in Section 4.2. Between each step of the sequential extraction, the sample was rinsed by extracting with 10 ml distilled water for fifteen minutes and the supernatant liquid was discarded as outlined in the method of Quevauviller *et al.* (1994).

**Table 7.1** The extraction times and volumes of the extracting solutions used in estimating the water soluble, exchangeable, acid-soluble elements from 0.6 g of a material

| Fractions | Reagents and volume | Extraction time |
|---|---|---|
| **Water soluble** | Distilled water (30 ml) | 1 hour |
| **Exchangeable** | 1 M ammonium nitrate (15 ml) | 30 minutes |
| **Acid-soluble** | 0.11 M acetic acid (24 ml) | 16 hours |

## 7.3 Results

### 7.3.1 Ammonium nitrate extraction

The concentration of elements found in single batch ammonium nitrate extraction (BEP-AN) was compared to the sum of the concentrations of elements extracted by water and ammonium nitrate extraction applied in sequential extraction (SEP-AN). The elements which were below detection were not plotted; this occurred where elements were detected for some materials but below detection for others. The concentration of Ca, as postulated, was comparable between SEP-AN and BEP-AN for all materials, except the EW (Figure 7.1b). Similar results were found for Co for the EW and the EW treated soils (Figure 7.1c).

The results which deviate from what was postulated can be categorised into two. The first category is where the concentrations of elements were higher in BEP-AN compared to SEP-AN. This was the case for Mg and Mn in both the EW treated soils and the SS treated soils, and also for Mg in the SS (Figure 7.1). The same trend was observed for S in the SS, SS treated soils, Ia soil, and the EW. Higher concentrations in the BEP-AN compared to the SEP-AN was pronounced for Ca and S in the EW and Al for the Ia soil.

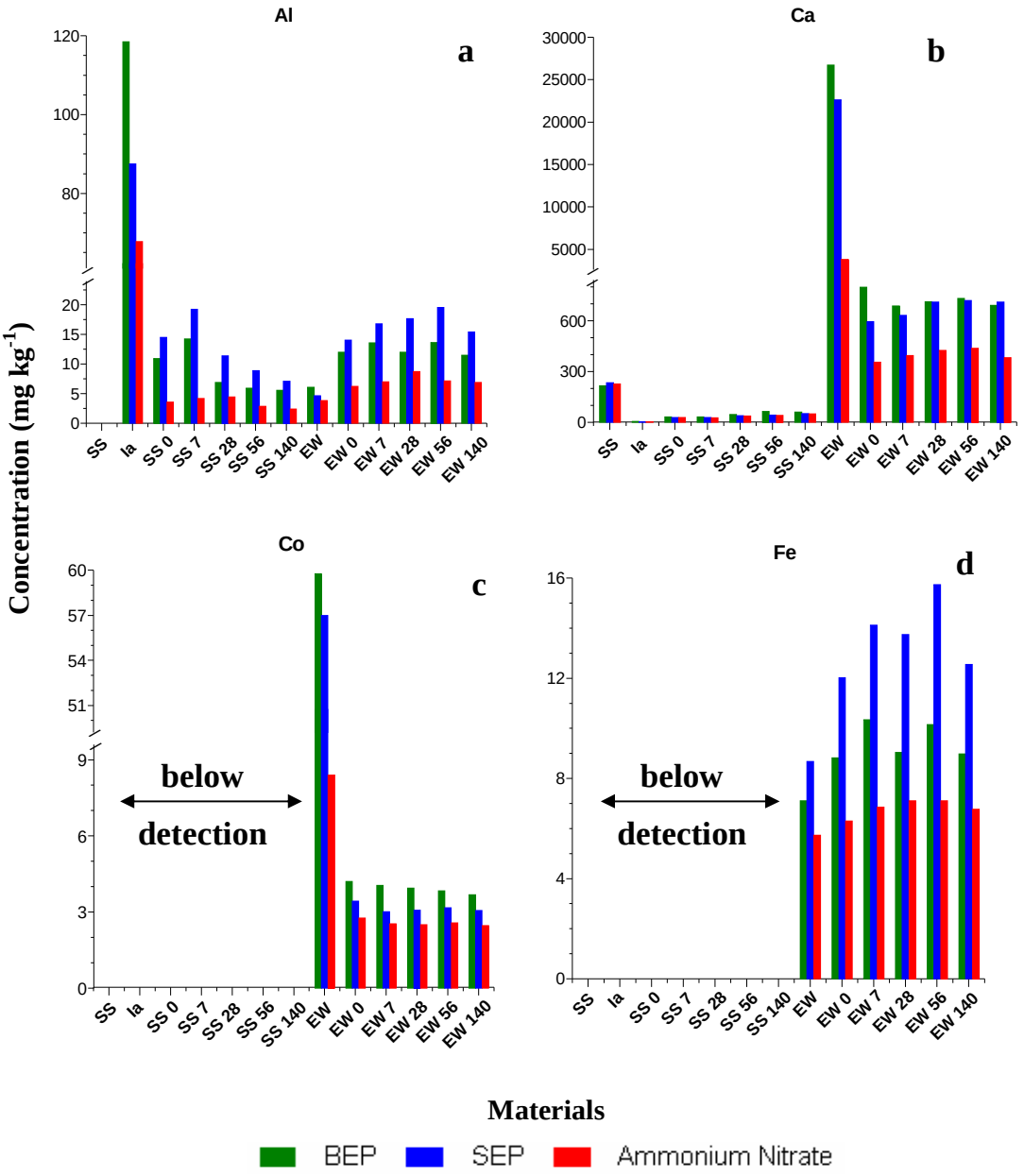



**Figure 7.1** A comparison in the concentration of (a) Al, (b) Ca, (c) Co (d) Fe, (e) Mg, (f) Mn, and (g) S between sequential (SEP-AN) and batch (BEP-AN) ammonium nitrate extraction from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by ammonium nitrate after water extraction (red bars) was added to the graph to show the contribution of ammonium nitrate on SEP-AN.

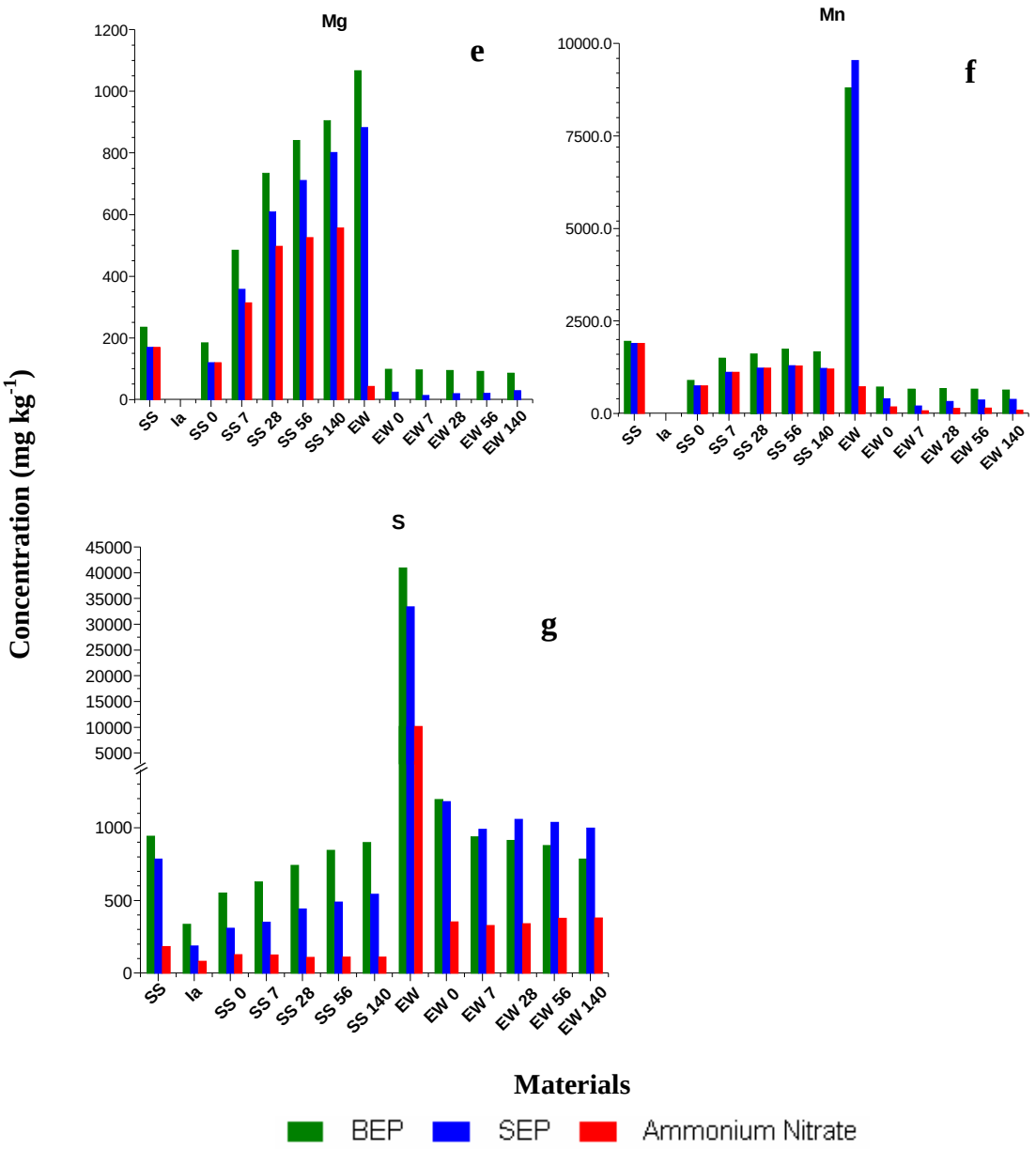



**Figure 7.1(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co (d) Fe, (e) Mg, (f) Mn, and (g) S between sequential (SEP-AN) and batch (BEP-AN) ammonium nitrate extraction from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by ammonium nitrate after water extraction (red bars) was added to the graph to show the contribution of ammonium nitrate on SEP-AN.

The second category is where the concentrations of elements were higher in the SEP-AN than in the BEP-AN. This behaviour was observed for Fe in the EW and the EW treated soils (Figure 7.1d) and Al in both the EW and the SS treated soils (Figure 7.1a). Similar trends were observed for Mn in the EW and S in the EW treated soils.

7.3.2 Acetic acid extraction

A comparison was also made between the concentrations of elements found in single acetic acid (BEP-AA) and the sum of water, ammonium nitrate, and acetic acid extraction applied in sequential extraction (SEP-AA). The elements which were below detection were not plotted; this occurred where elements were detected for some materials but below detection for others.

The comparison between single batch and sequential acetic acid extraction can be categorised into three. The first category is where the concentrations of elements were comparable between BEP-AA and SEP-AA. This was observed for Al, Mg, and Mn in the SS and the SS treated soils (Figure 7.2). Similar trends were observed for Mg in the EW; Fe in the EW treated soils; and Ca in both the SS and the EW treated soils (Figure 7.2).

The second category is where the concentrations of elements were higher in the BEP-AA compared to the SEP-AA. This was observed for Mg and Mn in the EW treated soils and Mn and Co in the EW (Figure 7.2). Similar results were found for Al in the Ia soil, and S in the SS, Ia soil, and the SS treated soils (Figure 7.2).

The third category is where higher concentrations of elements were found in the SEP-AA than in the BEP-AA. This category included Al and S in the EW and the EW treated soils and Zn in the EW (Figure 7.2). Similar results were found for Ca and Fe in the SS and Ca in the Ia soil (Figure 7.2).

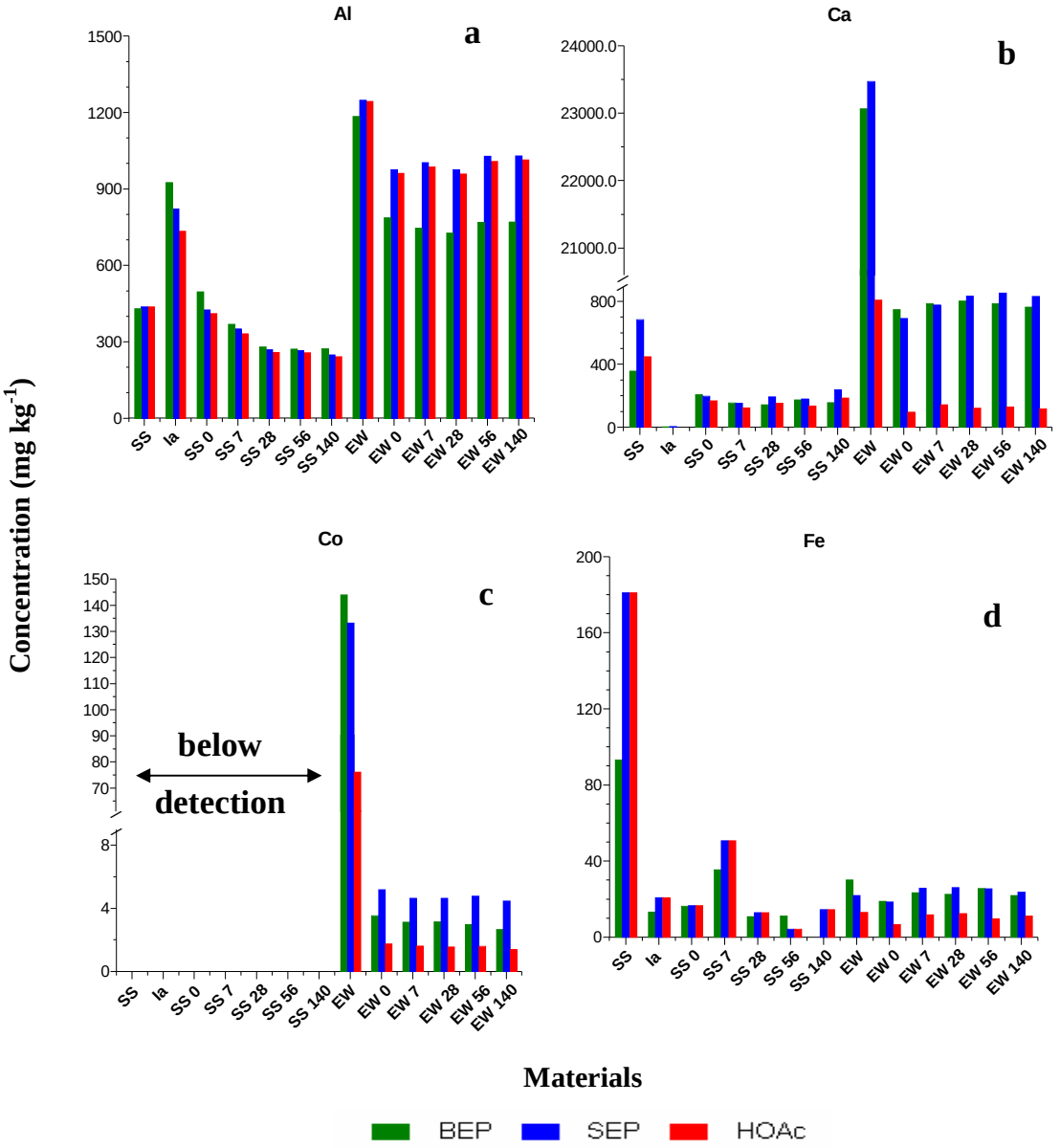



**Figure 7.2** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Fe, (e) Mg, (f) Mn, (g) S, and (h) Zn between sequential (SEP-AA) and batch (BEP-AA) acetic acid extraction from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by acetic acid (HOAc) after water and ammonium nitrate extraction (red bars) was added to the graph to show the contribution of HOAc on SEP-AA.

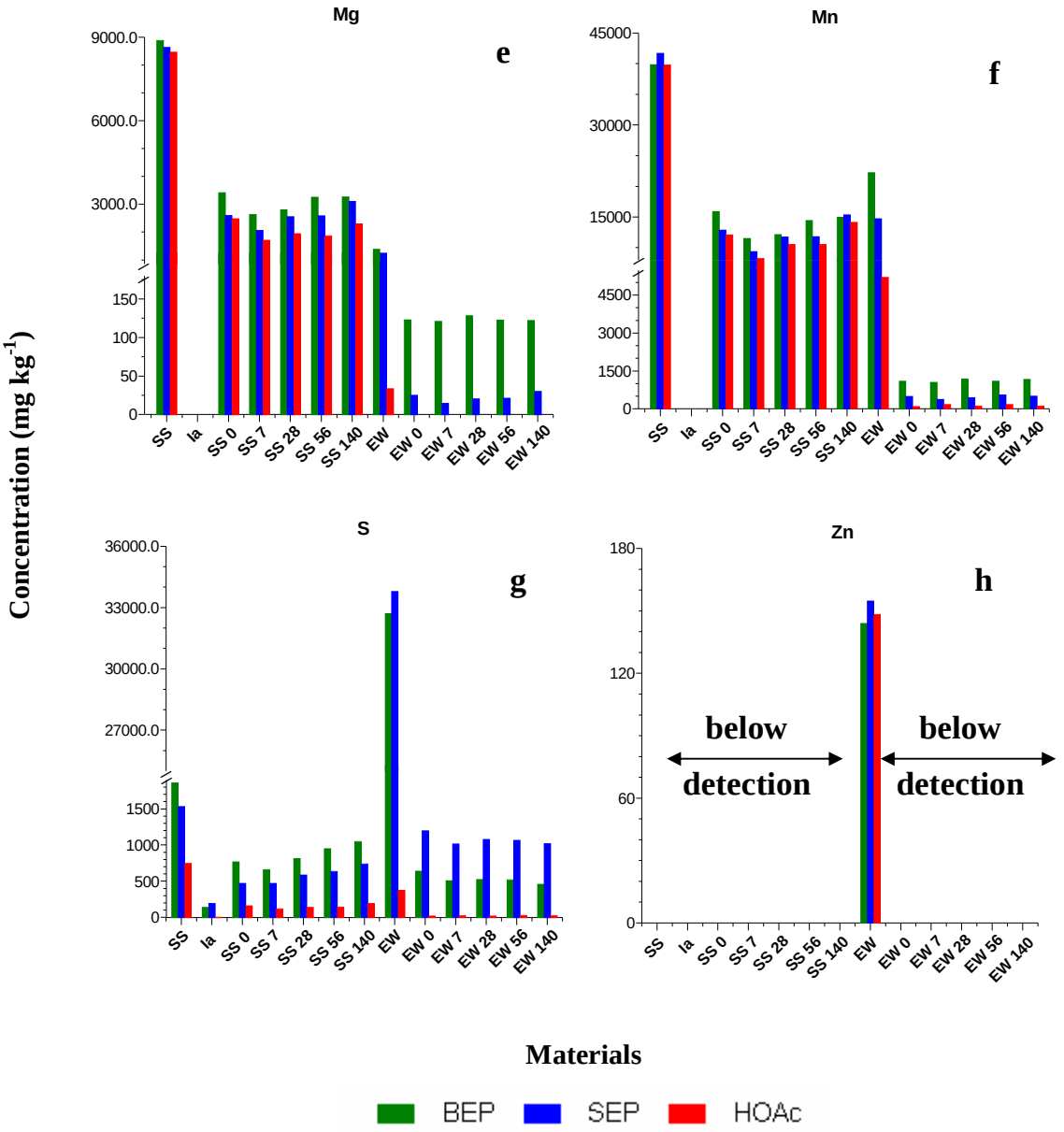



**Figure 7.2(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Fe, (e) Mg, (f) Mn, (g) S, and (h) Zn between sequential (SEP-AA) and batch (BEP-AA) acetic acid extraction from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by acetic acid (HOAc) after water and ammonium nitrate extraction (red bars) was added to the graph to show the contribution of HOAc on SEP-AA.

## 7.4 Discussions

The results above suggest that the comparison between single and sequential extractions is affected by the interaction between the elements of interest, the extracting reagent, and the material extracted. This interaction resulted in three categories where the concentrations of elements in single extractions were comparable, higher, and lower compared to those in sequential extraction.

The higher concentration of elements in single extraction compared to sequential extraction was not expected. This may, however, indicate that transformation of elements into less available forms occurs during sequential extraction. It might also indicate that there is a loss of sample during the rinsing step as the rinsing solution was discarded. However, it is doubted that rinsing could have released elements which were not extracted by the previous extraction as the rinsing is ought to remove the occluded solution only.

Readsorption of released elements and precipitation of secondary minerals are the two possible mechanisms which may result in the reduced availability of elements during sequential extraction. There were no significant differences in the pH between single and sequential extraction which eliminates the possibility of forming secondary minerals.

The readsorption is most likely to occur because the studied materials have high a sorption capacity and, as a result, elements can be readsorbed on organic matter, silicates, and Fe-Mn oxides during water extraction. The readsorption of elements during water extraction is not a new concept as Pratt (1965) recommended that water soluble elements should not be removed before the assessment of the exchangeable fraction. The exchangeable fraction should then be assessed by subtracting the results of a water extraction from the results of the exchangeable fraction determined as a single batch extraction. This recommendation was based on the fact that water extraction will cause readsorption of released divalent and trivalent cations which will reduce their availability (Pratt, 1965). Schramel *et al.* (2000) have also indicated that the simultaneous determination of the water soluble and exchangeable fractions using salt

solutions will minimise the readsorption of released elements. However, no indication has been made on how strong the readsorbed elements are retained on mineral and organic matter surfaces after water extraction. Nevertheless, the results of acetic acid extraction indicates that readsorbed elements are strongly retained on the Ia soil, the EW, and the EW treated soils as they were not released even by acetic acid.

The higher concentrations of elements in sequential extraction compared to single extraction might have resulted from two mechanisms. The first mechanism would be the saturation of extracting solution during single extraction. The saturation of the extracting solution would be favoured by high salt concentration of the EW. When the extracting solution is saturated readsorption of released elements and precipitation of secondary minerals may occur. As mentioned earlier, the possibility of forming secondary minerals for one technique of extraction and not the other is unlikely. The readsorption is most likely to occur, particularly for Mn, S, and Zn in the EW and the EW treated soils. Nevertheless, higher solution:solid ratio can be used to avoid the saturation of the extracting solution.

The second mechanism is the continued desorption of elements and dissolution of amorphous minerals due to increased extraction volume and extraction time when reagents are applied in sequential extraction. Enhanced desorption of elements or dissolution of amorphous minerals can arise when each reagent used in sequential extraction exposes fresh surfaces. The amorphous minerals reported to form when the wastes interact with the Ia soil (Chapter 6) may be dissolved due to increased extraction volume and extraction time, particularly for the SS and the SS treated soils. The increasing sorption of S due to decreasing pH when the EW was applied to Ia soil was also reported. This would imply that higher S in sequential extraction is released as results of continued desorption from water to ammonium nitrate to acetic acid extraction. Whereas higher Al and Fe in sequential extraction would be caused by continued dissolution of amorphous minerals. This may also be supported by ammonium nitrate's (roughly 50%) contribution to SEP-AN (Figure 7.1 a, d, and g) and more than 50 % contribution of acetic acid to SEP-AA (Figure 7.2 a, d, and g) for Al, Fe, and S. Furthermore, the SS has low surface area (Section 3.3.2.1) and may limit the

release of elements when applying ammonium nitrate and acetic acid as single batch extractions. The higher concentrations of Ca and Fe in the acetic acid (applied after water and ammonium nitrate extraction) extraction for the SS may also support the fact that the previous extractions exposes fresh surfaces which enhances the release of elements. These results may also indicate the release of elements from the non targeted fractions.

## 7.5 Conclusions

The need to include the water soluble and exchangeable fractions in the BCR sequential extraction protocol was investigated by comparing the concentration of elements extracted by batch and sequential extraction. Both techniques were found to have limitations.

The limitation of the batch extractions were the possibility of saturation of the extracting reagent when elements are present in high concentrations (e.g. Mn in the EW) and the material has a high content of soluble salts. The main limitation of the sequential extraction was readsorption of elements (such as Mg and Mn in the EW treated soils) during water extraction. This may question the water rinsing step in sequential extractions as it can potentially induce readsorption of released elements. This can be minimised measuring water extractable elements separately from the exchangeable fraction (and other fractions measured in sequential extractions) and by using a dilute salt solution in the rinsing step. The correction for the water soluble elements should be made by subtracting the concentration of water soluble elements from the concentration of elements extracted by single ammonium nitrate extraction. However, the release of elements from acetic acid after ammonium nitrate extraction only was not investigated. This may have the advantage of minimising the readsorption of elements yet providing a successive release of elements. Hence, it postulated that an additional step of the exchangeable fraction may have positive effect on the BCR sequential extraction. The second limitation of the sequential extractions is that they can cause continued desorption of elements or dissolution of amorphous minerals. This may result in release of elements from non targeted fractions.

# CHAPTER 8

# A COMPARISON BETWEEN THE SEQUENTIAL AND BATCH EXTRACTIONS FOR THE BCR SEQUENTIAL EXTRACTION PROTOCOL

## 8.1 Introduction

Sequential extraction protocols (SEP) provide an indication of the amount of an element retained in various reservoirs which could be released when there are changes in soil solution chemistry, notably pH or Eh (Pueyo *et al.*, 2003). However, long extraction times make SEP undesirable to use. In an attempt to reduce the long extraction time, the use of ultrasound assisted extraction has been suggested (Perez-Cid *et al.*, 1998). When this technique is applied to the BCR SEP the extraction time is reduced from 51 hours to 22 minutes. Perez-Cid *et al*. (1998) found that the results obtained when this technique was applied to sewage sludge were comparable to those obtained using the standard BCR SEP. However, not all laboratories can afford the equipment required. Another attractive approach involves the use of the same reagents and operating conditions as in a sequential extraction, but using a separate sample for each reagent. Albores *et al.* (2000) found that when this 'batch' approach was applied to the BCR extraction protocol the operation time was reduced from 51 hours to 16 hours and the results were comparable between sequential and batch extraction.

There are limited studies that investigate this alternative approach to the BCR SEP on different materials. Thus, the objective of this investigation was to compare the standard BCR SEP to batch extraction (using reagents and operating conditions) on pure wastes, uncontaminated soil, and waste treated soils.

## 8.2 Materials and Methods

Two wastes and one uncontaminated soil (EW, SS and the Ia soil used in Chapter 3) and soil waste mixtures (used in Chapter 6) were used in this investigation. The BCR sequential extraction was carried out as described in Section 5.2. For the batch extractions each reagent was used to extract a separate sample, using the same

soil:solution ratios and extraction times for each reagent as presented in Table 5.1. Solutions were separated, stored, and analysed for pH and elemental concentration as was described in Section 4.2. Between each step of the sequential extraction, the sample was rinsed by extracting with 10 ml distilled water for fifteen minutes and the supernatant liquid was discarded (Quevauviller *et al.*, 1994).

A separate set of samples were also extracted. Their solid residues were retained after each extraction, for both batch and sequential extraction, for a solid phase analysis. The mineralogy of these residues was determined on randomly oriented powder samples by XRD (Philips PW1050). Solid residues were also examined using environmental scanning electron microscopy (ESEM, Philips XL 30). Qualitative chemical composition was determined by energy dispersive X-ray microanalysis (EDX) and the data interpreted using the EDAX® Phoenix software (Revision 3.2).

The differences between these extraction methods compared using a t-test (Microsoft excel).

## 8.3 Results and Discussion

### 8.3.1 The hydroxylammonium chloride extraction

Acetic acid results were not included in this discussion because acetic acid is the first reagent in the BCR SEP, hence whether used as a batch or in sequential extraction the method is still the same.

Batch hydroxylammonium chloride (BEP-HAC) extraction was compared to the sequential HAC (SEP-HAC) extraction (Figure 8.1). The concentrations for SEP-HAC, which were used for comparison, were obtained by adding the concentration of elements extracted by acetic acid and HAC in sequential extraction. The results of these two methods were comparable for Ca, Co, Fe, Mg, Mn, and S for the EW treated soils (Figure 8.1). The same trend was observed for Fe in the Ia soil; Mg in the EW; and Mn in the EW.

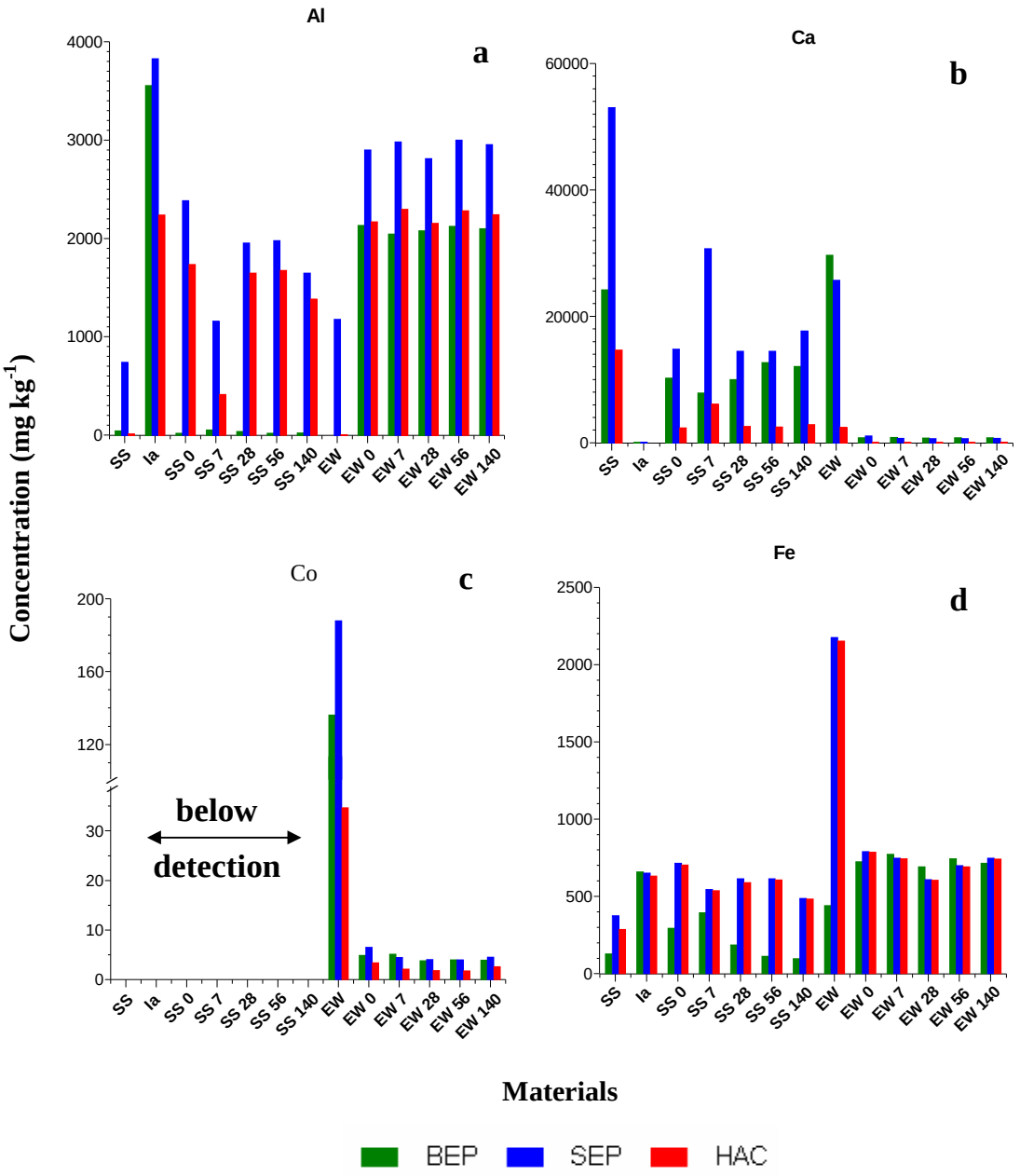



**Figure 8.1** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Fe, (e) Mg, (f) Mn, (g) Pb, (h) S, and (i) Zn between sequential (SEP-HAC) and batch (BEP-HAC) hydroxylammonium chloride from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by HAC after acetic acid extraction (red bars) was added to the graph to show the contribution of HAC on SEP-HAC.

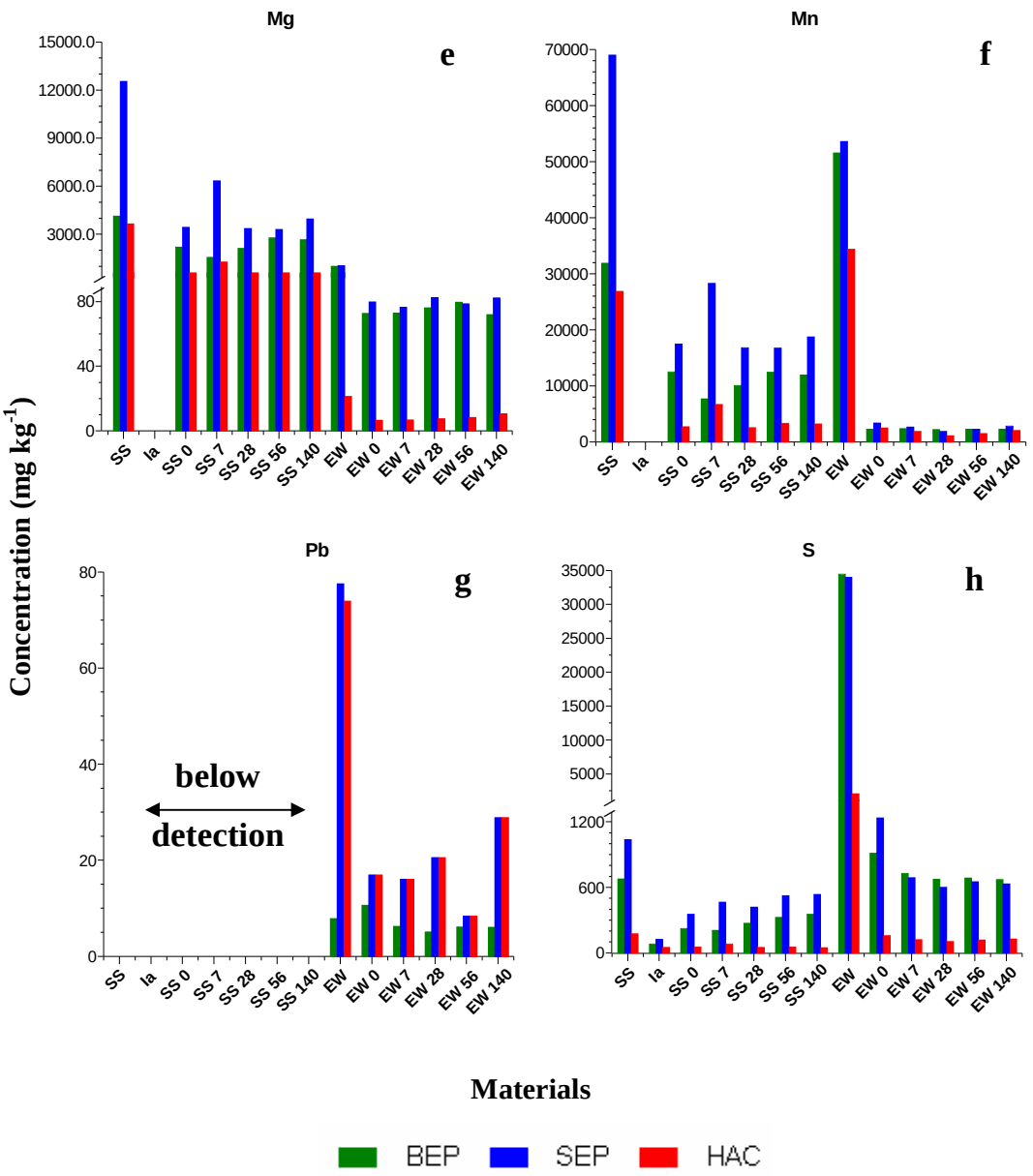



**Figure 8.1(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Fe, (e) Mg, (f) Mn, (g) Pb, (h) S, and (i) Zn between sequential (SEP-HAC) and batch (BEP-HAC) hydroxylammonium chloride from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by HAC after acetic acid extraction (red bars) was added to the graph to show the contribution of HAC on SEP-HAC.

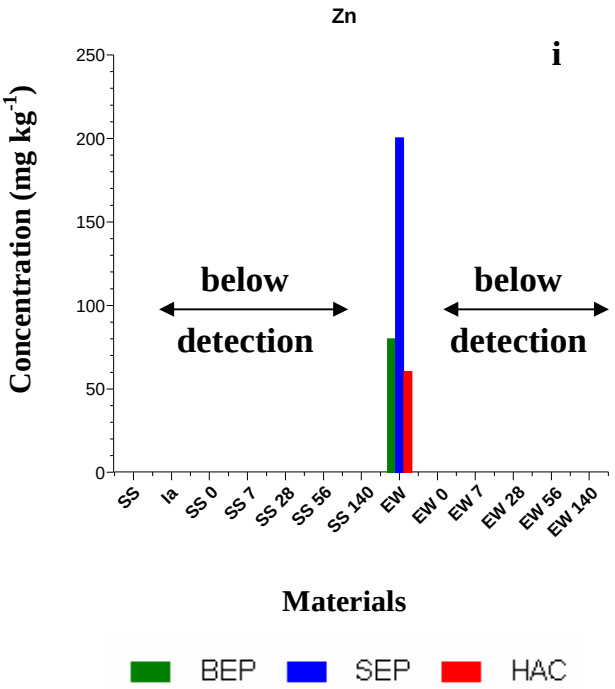



**Figure 8.1(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Fe, (e) Mg, (f) Mn, (g) Pb, (h) S, and (i) Zn between sequential (SEP-HAC) and batch (BEP-HAC) hydroxylammonium chloride from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by HAC after acetic acid extraction (red bars) was added to the graph to show the contribution of HAC on SEP-HAC.

Generally, SEP-HAC had higher concentration of elements compared to BEP-HAC for the SS and the SS treated soils (Figure 8.1). The same trend was observed for Al in the Ia soil and the EW treated soils; Co in the EW; Fe in the EW; Pb in the EW and the EW treated soils; and Zn in the EW. These results indicated that a single HAC extraction does not extract the same amount elements extracted by acetic acid and HAC in sequential extraction. This might be caused by some mechanisms which are different for the various materials studied here. These mechanisms occur during single HAC extraction and are precipitation of secondary minerals for the SS and the SS treated soils; readsorption of released elements for the EW and the EW treated soils; minimal

dissolution of mineral for the EW and the Ia soil; and transformation elements for the EW. Continued desorption of elements and dissolution of amorphous minerals due to increased extraction volume and extraction time when reagents are applied in sequential extraction may have occurred also.

The continued desorption of elements and dissolution of amorphous minerals can be caused by the previous (acetic acid) extraction exposing fresh surfaces. The ‘exposed surfaces’ after acetic acid extraction are most likely to occur in the case of the SS and the SS treated soil because the SS has low surface area and to a lesser degree in the EW and the EW treated soils. If the acetic exposed fresh surfaces then the contribution of HAC to SEP-HAC is expected to be more than 50 % which was the case for Al, Co, Fe, Mg, and Pb. Another possibility with ‘exposed surfaces’ is the partial dissolution of minerals by acetic acid, particularly for the SS where the predominant mineral is unstable at low pH of the extracting solution. When partial dissolution occurred during the acetic acid extraction then the acetic acid would have a considerable contribution to SEP-HAC which was the case for Ca, Mn, S, and Zn. The considerable contribution of acetic acid to the concentration of Ca and Mn in the SEP-HAC might support the partial dissolution of glaucochroite during the acetic acid extraction. The evidence suggesting the partial dissolution of minerals by acetic acid extraction and exposed fresh surfaces after acetic acid extraction might be indicating that partial dissolution of mineral would results in exposed fresh surfaces.

Readsorption of released elements and formation of secondary minerals may occur as a result of saturation of the extracting solution. The saturation of the extracting solution could be caused by the high soluble salts and high concentration of elements in extracting solution which is most likely to occur when HAC is applied as single extraction. Released elements would get readsorbed on the surfaces of the newly formed amorphous minerals and partially dissolved oxides. The formation of amorphous minerals is facilitated by elevated pH. High pH in BEP-HAC (Appendix 8.1) would support the formation of amorphous minerals during single extraction for the SS and SS treated soils. The higher concentration of Ca, Mg, and Mn in SEP-HAC than in BEP-HAC for the SS might be reflecting the saturation of extracting solution which resulted in readsorption of these elements during single HAC extraction. The formation of

amorphous minerals can contribute in the incomplete dissolution of minerals (Appendix 3.6).

Incomplete dissolution of minerals could have occurred in both single and sequential extractions. However, as mentioned earlier, for sequential extraction the dissolution of minerals is improved. The dissolution of minerals in single HAC extraction would then be minimal. The incomplete dissolution is most likely a result of the strength of the extracting solution which cannot completely dissolve the crystalline oxide minerals. The solution of 0.1 M HAC was considered to cause incomplete dissolution of Al and Fe oxides/hydroxides when applied as single extraction. Bermond (2001) also questioned the ability of 0.1 M HAC to dissolve crystalline oxides. Neaman *et al*. (2004b) reported that 0.1 M HAC, used in this experiment, released about 95, 12, and 3 percent of Mn, Al, and Fe respectively. Feng-Mei *et al*. (2006) reported a recovery of 86 % for Mn oxides when 0.1 M HAC was used but this reagent dissolved about 1 % of organic matter and 20 % of Fe oxides. It was thus proposed that the lower concentrations of Al and Fe in BEP-HAC for the EW and EW treated soils were due to incomplete dissolution of crystalline Al and Fe oxides/hydroxides. This is confirmed by composition of the solid residue after HAC extraction. The EDX analysis shows that there was a high content of Al and Fe on the EW residue retained for BEP-HAC compared to SEP-HAC (Appendix 8.2). However, there were no differences observed in the XRD traces for the residues retained after HAC extraction for sequential and batch extractions (Appendix 8.3). This is probably because the difference between these two techniques was too small to be detected on the XRD. Nevertheless, these results might be indicating that single 0.1 M HAC is not releasing both acid-soluble and reducible elements which are released by acetic acid and HAC when applied in sequential extraction. The use of acetic acid and HAC in sequential extraction has the advantage of using two aggressive extractant and, technically, doubling the volume of the extracting solution.

The higher concentration of Co, Pb, and Zn in SEP-HAC than in BEP-HAC for EW and EW treated soils might have also been due to the readsorption of these elements on partially dissolved Al and Fe oxides/hydroxides and on organic matter. These elements have high affinity for Al, Fe, Mn oxides and organic matter (McBride; 1994). Several

authors have indicated that organic matter, Fe-Mn oxides and hydroxides, changes in pH during extraction, and incomplete dissolution of hydrous oxides are the main factor contributing to the readsorption of released elements (Raksasataya *et al.*, 1996; Gleyzes *et al.*, 2002). Bermond (2001) confirmed the readsorption of heavy metals through the application of $BaClO_4$ after a single extraction with HAC and also found that the readsorption was affected by the final extraction pH. The readsorption became substantial at pH above 2.5 and was almost complete in the pH range of 6-7. The pH above 2.5 in the single HAC extraction supports that substantial readsorption of elements could have occurred (Appendix 8.1).

Transformation of elements (Co, Fe, and Pb) in the EW during single extraction could occur through oxidising mechanisms. Comparable concentrations of Mn between single and sequential HAC extraction might suggests that Mn (III) present as a salt in jacobsite (Appendix 3.2) is oxidising these elements into less soluble forms. Manganese salts containing Mn (III) could have been removed by acetic acid before redox conditions were induced by HAC extraction, which will minimise the oxidation of these elements. Manganese (III) is a known powerful oxidising agent and can oxidise $Co^{2+}$ into $Co^{3+}$, $Fe^{2+}$ into $Fe^{3+}$, and $Pb^{2+}$ into $Pb^{4+}$ which will result in low solubility of these elements (McBride, 1994). The $Fe^{3+}$ would precipitate out as magnetite (Appendix 3.2) and $Co^{3+}$ and $Pb^{4+}$ would be strongly adsorbed on partially dissolved oxide minerals.

8.3.2 The hydrogen peroxide extraction

A comparison between SEP-$H_2O_2$ and BEP-$H_2O_2$ was also made (Figure 8.2). The concentrations for SEP-$H_2O_2$, which were used for comparison, were obtained by adding the concentration of elements extracted by acetic acid, HAC and $H_2O_2$ in sequential extraction. The results of these two methods were comparable for Al, Ca, Co, and Mg, for the EW (Figure 8.2). The same trend was observed for Ca in the SS treated soils and EW treated soils; Mg in the SS treated soils; Mn in the SS and the SS treated soils; and S in the SS in the Ia soil, SS treated soils and the EW treated soils.

Similarly to the HAC extraction, the concentration of Al was higher in SEP-$H_2O_2$ than in BEP-$H_2O_2$ for the SS, Ia soil, SS treated soils and the EW treated soils. The same trend was observed for Fe in the Ia soils, SS treated soils, EW, and the EW treated soils;

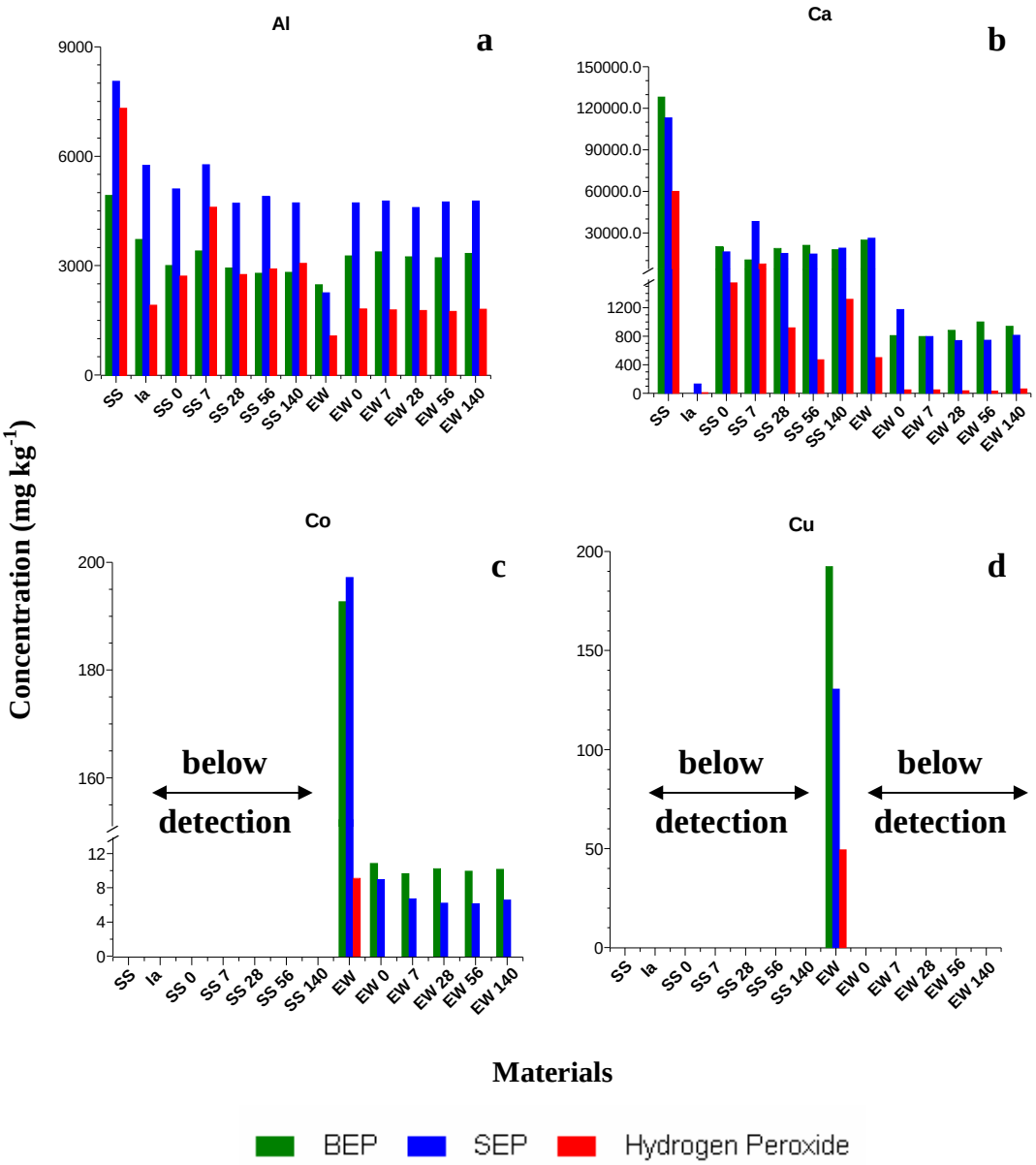



**Figure 8.2** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Cu, (e) Fe, (f) Mg, (g) Mn, (h) Pb, (i) S, and (j) Zn between sequential (SEP-$H_2O_2$) and batch (BEP-$H_2O_2$) hydrogen peroxide from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by hydrogen peroxide after acetic acid and hydroxylammonium chloride extraction (red bars) was added to the graph to show the contribution of $H_2O_2$ on SEP-$H_2O_2$.

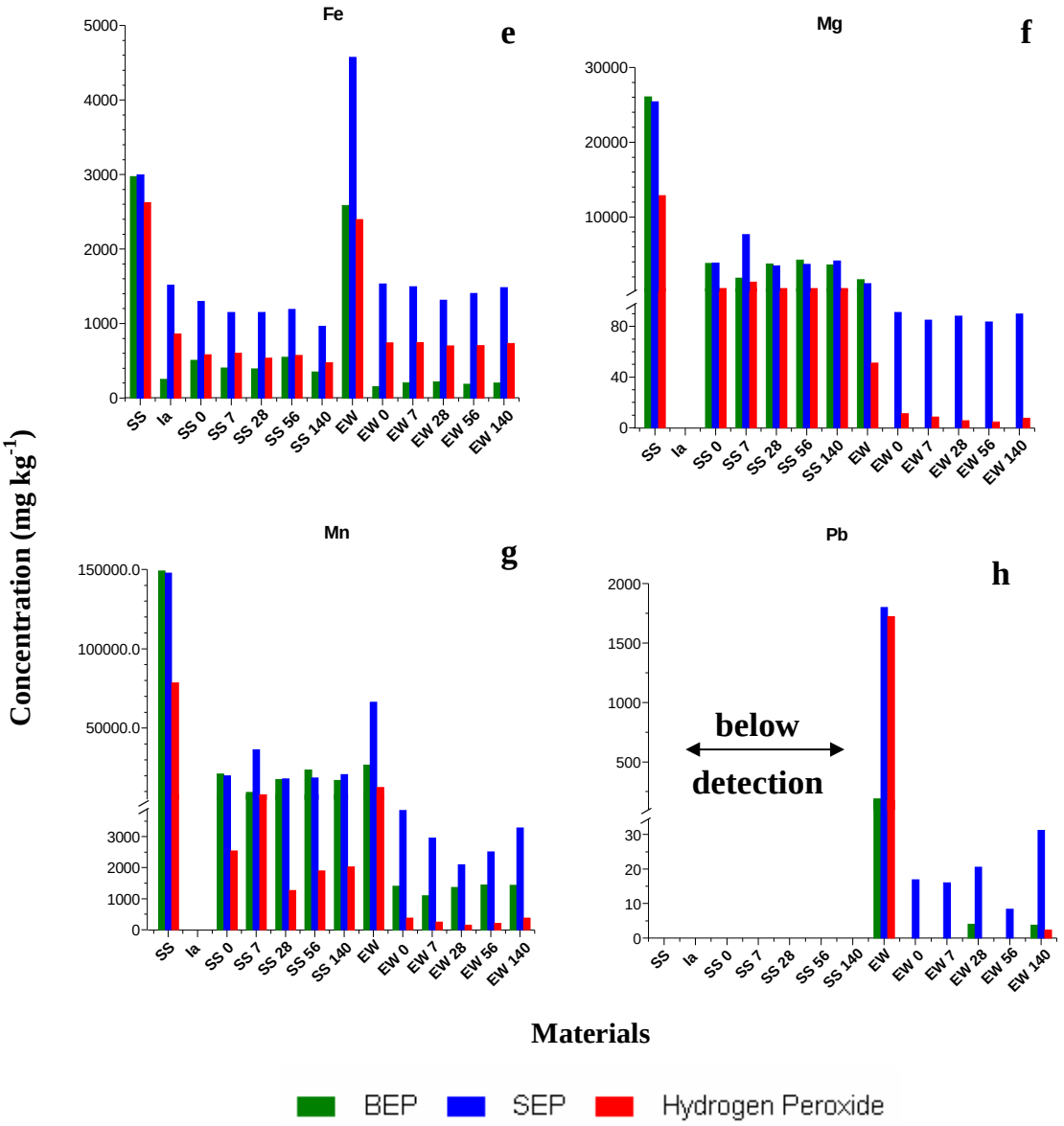



**Figure 8.2(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Cu, (e) Fe, (f) Mg, (g) Mn, (h) Pb, (i) S, and (j) Zn between sequential (SEP-$H_2O_2$) and batch (BEP-$H_2O_2$) hydrogen peroxide from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by hydrogen peroxide after acetic acid and hydroxylammonium chloride extraction (red bars) was added to the graph to show the contribution of $H_2O_2$ on SEP-$H_2O_2$.

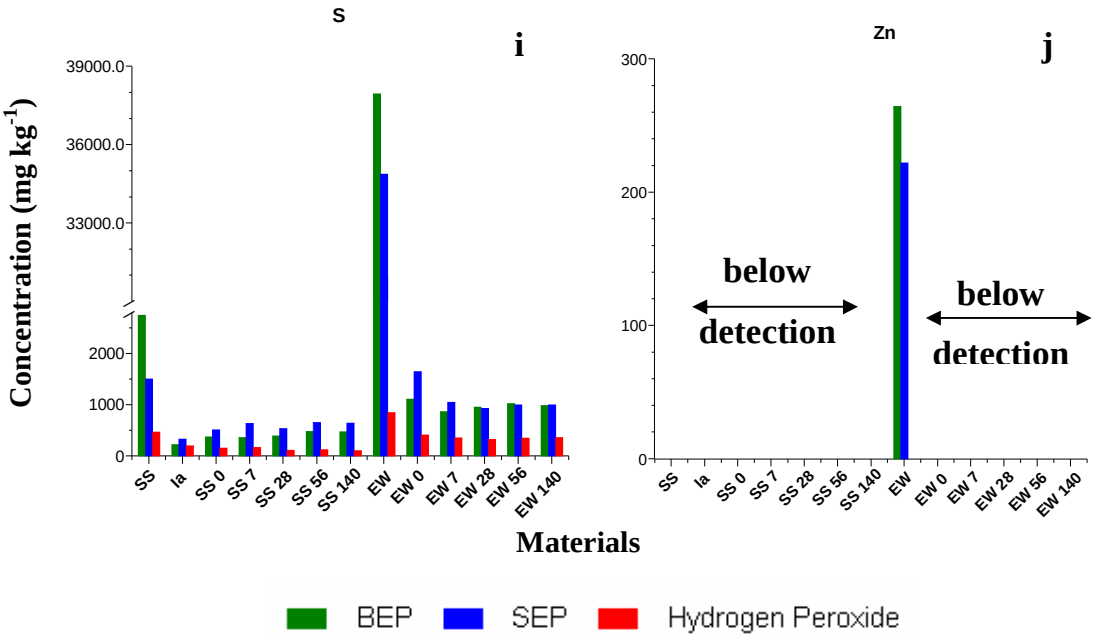



**Figure 8.2(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Cu, (e) Fe, (f) Mg, (g) Mn, (h) Pb, (i) S, and (j) Zn between sequential (SEP-$H_2O_2$) and batch (BEP-$H_2O_2$) hydrogen peroxide from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by hydrogen peroxide after acetic acid and hydroxylammonium chloride extraction (red bars) was added to the graph to show the contribution of $H_2O_2$ on SEP-$H_2O_2$.

Mg in the EW treated soils; Mn in the EW and EW treated soils; and Pb in the EW and the EW treated soils. The same mechanisms that resulted in a higher concentration of elements in the SEP-HAC than in BEP-HAC (i.e. continued dissolution of minerals and exposed surfaces for sequential extraction and precipitation of amorphous minerals, incomplete dissolution of Al and Fe oxides/hydroxides, and readsorption of released elements for single extraction) could be operative even with $H_2O_2$.

However, the formation of amorphous minerals might be less effective, because of low final extraction pH's (Appendix 8.1). The formation of amorphous minerals can results

in incomplete dissolution of minerals, particularly for the SS and the SS treated soils (Appendix 3.6). The comparable concentrations of Ca, Mg, and Mn in the SS and the SS treated soils suggest that the degree of glaucochroite dissolution between SEP-$H_2O_2$ and BEP-$H_2O_2$ was similar. This suggests that $H_2O_2$, when applied as single extraction, is aggressive enough to cause the dissolution of glaucochroite as would have been caused by acetic acid, HAC, and $H_2O_2$ together. The XRD traces also showed substantial dissolution of glaucochroite (glaucochroite peaks decreased by more 80%) for both sequential and batch $H_2O_2$ extractions suggesting a more complete dissolution of glaucochroite. It also suggests that ammonium acetate has enough complexing ability to retain released elements in solution and inhibit the formation of secondary minerals. This is in accordance with earlier discussion (Appendix 3.6) that formation of secondary minerals is inhibited by complexing agents which enhances the dissolution of minerals.

The high concentrations of Al and Fe in the SEP-$H_2O_2$ than BEP-$H_2O_2$ for the SS and SS treated soils remains a question. These elements were released mainly in the RES fraction for both the SS and the Ia soils (Chapter 5). These results may then suggest that $H_2O_2$ attacks crystalline materials due increase in surface area when fresh surfaces are exposed. Tessier *et al*. (1979) has also reported the dissolution of crystalline material by $H_2O_2$ when applied in sequential extraction.

The incomplete dissolution of minerals in the EW and the EW treated soils could have also occurred in the case of BEP-$H_2O_2$. This may be supported by high content of Al and Fe, observed with the EDX analysis, on the EW residue retained for BEP-$H_2O_2$ compared to SEP-$H_2O_2$ (Appendix 8.2). However, no differences were observed in the XRD traces for residues left after single and sequential $H_2O_2$ extraction (Appendix 8.4).

Jacobsite dissolution may results in the formation of $Fe_2O_3$ (Section 5.3.1). This may be formed during reductive dissolution of jacobsite when HAC is applied is sequential extraction. When $H_2O_2$ is applied after HAC extraction then partial dissolution of the secondary mineral may occur. However, in the case of single $H_2O_2$ extraction $Fe_2O_3$ is formed and is not partially dissolved due to either limited solution or limited acidity. This may explain the high concentration of Al, Fe, Mg, Mn, and Pb in SEP-$H_2O_2$ compared to BEP-$H_2O_2$. Several authors have indicated that crystalline Al and Fe

oxides/hydroxides are partially dissolved by $H_2O_2$ but amorphous minerals are completely dissolved (Ryan *et al.*, 2002; Neaman *et al.*, 2004a; Neaman *et al.*, 2004b).

The concentration of Cu, S, and Zn were higher in BEP-$H_2O_2$ than in SEP-$H_2O_2$ for the EW (Figure 8.2). The concentration of S was also higher in BEP-$H_2O_2$ than in SEP-$H_2O_2$ for the SS. This might be caused by the readsorption of these elements or formation of sulphide minerals during the HAC extraction step. However the formation of sulphides is unlikely as HAC could not dissolve crystalline Fe oxides. Hence, these elements could have been adsorbed on partially dissolved Fe-Mn oxides

8.3.3 The aqua regia extraction

The use aqua regia (BEP-AR) as a method to estimate the pseudo-total elemental concentration is a common practice. Another common practice is the summation of acid-soluble, reducible, oxidisable, and residual concentrations (SEP-AR) of elements to estimate the total content. In principle, these two methods should yield similar results, which was the case for most elements (Figure 8.3) with the exception of the few which will be discussed below. These results would be expected after some degree of comparability was observed between single and sequential extraction with $H_2O_2$. Since aqua regia is more aggressive than $H_2O_2$, then an even greater degree of comparability should results between single and sequential extraction for aqua regia.

The concentration of Al was higher in SEP-AR than in BEP-AR for the SS treated soils and the EW treated soils (Figure 8.3 a). The same trend was observed for Co in the SS and Ia soil; Cu in the SS, Ia soil, and the SS treated soils; Fe in the EW and the EW treated soils; Mn in the SS; Pb in the EW and the EW treated soils; and S in the SS and the EW. The same mechanisms that resulted in a higher concentration of elements in sequential extraction compared to single extraction (i.e. continued dissolution of minerals and exposed surfaces for sequential extraction and precipitation of amorphous minerals, incomplete dissolution of Al and Fe oxides/hydroxides, and readsorption of released elements for single extraction) may have contributed to the higher concentrations of these elements in SEP-AR compared to BEP-AR.

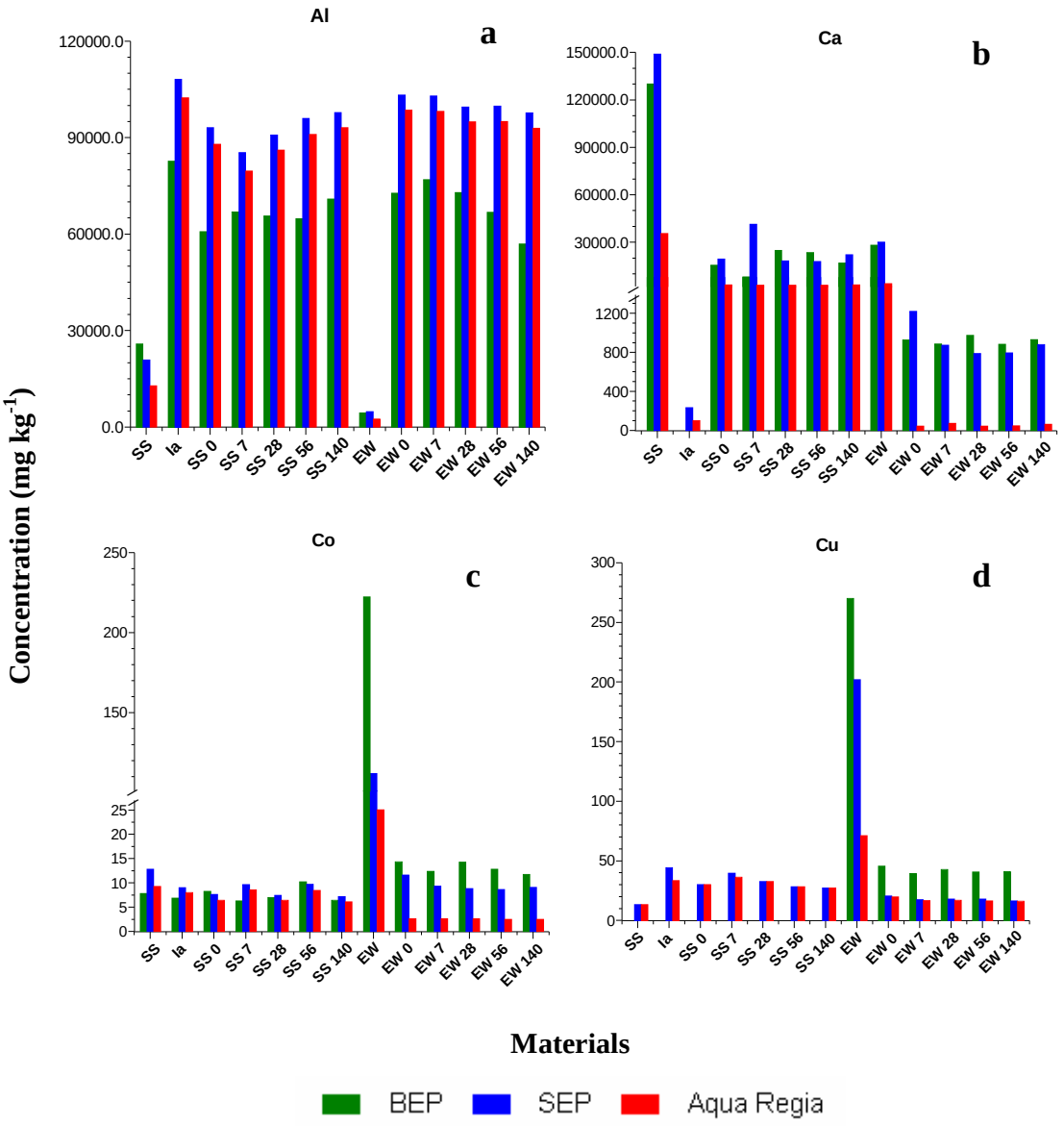



**Figure 8.3** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Cu, (e) Fe, (f) Mg, (g) Mn, (h) Pb, (i) S, and (j) Zn between summation (SEP-AR) and pseudo total (BEP-AR) methods of estimating total elemental content from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by aqua regia after acetic acid, hydroxylammonium chloride and hydrogen peroxide extraction (red bars) was added to the graph to show the contribution of aqua regia on SEP-AR.

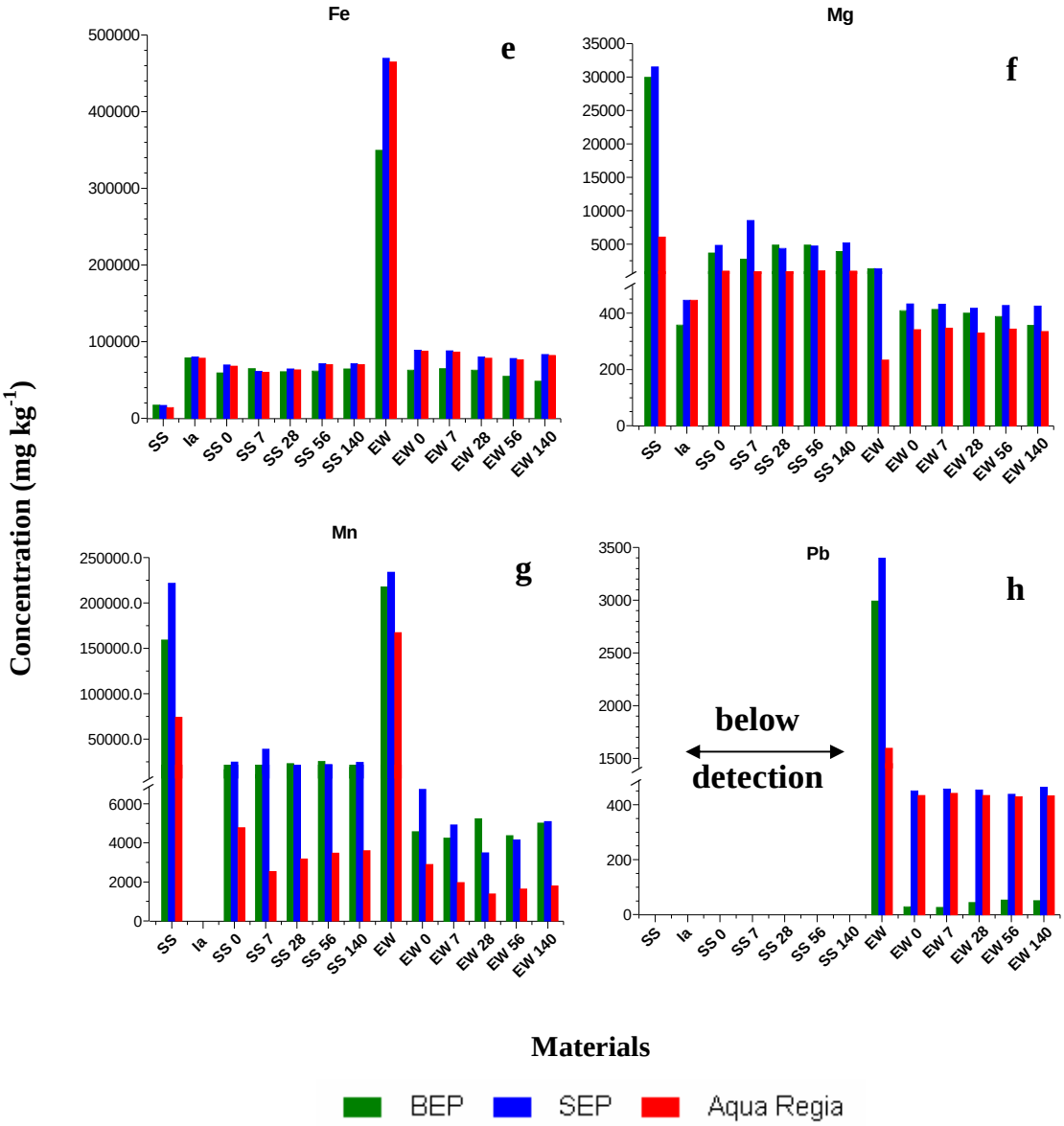



**Figure 8.3(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Cu, (e) Fe, (f) Mg, (g) Mn, (h) Pb, (i) S, and (j) Zn between summation and pseudo total methods of estimating total elemental content from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by aqua regia after acetic acid, hydroxylammonium chloride and hydrogen peroxide extraction (red bars) was added to the graph to show the contribution of aqua regia on SEP-AR.

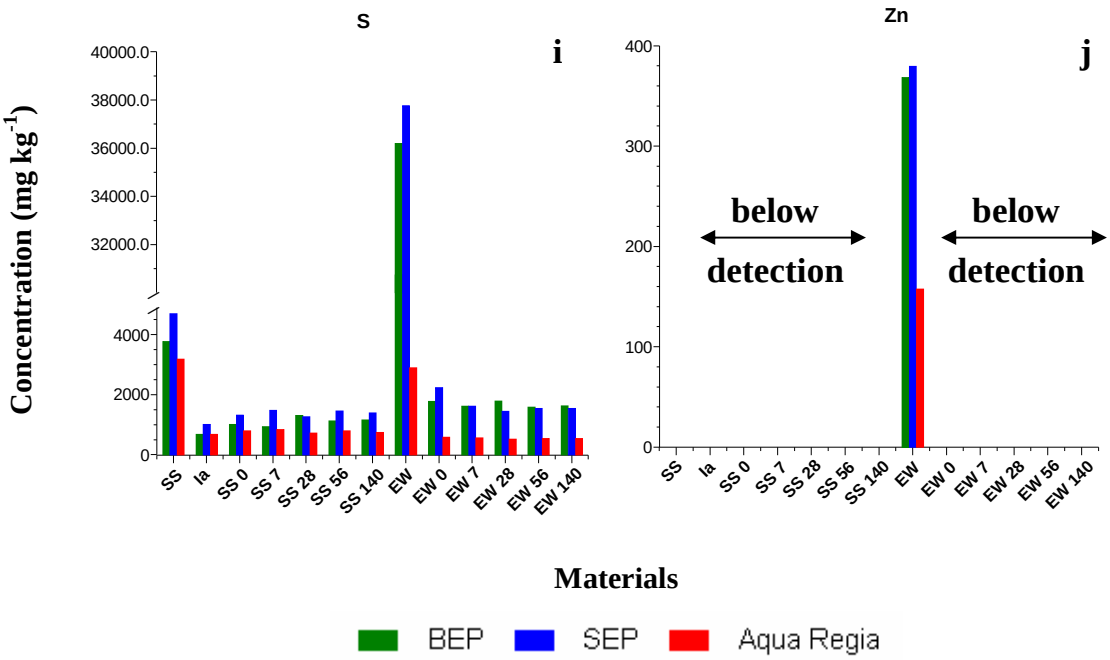



**Figure 8.3(cont)** A comparison in the concentration of (a) Al, (b) Ca, (c) Co, (d) Cu, (e) Fe, (f) Mg, (g) Mn, (h) Pb, (i) S, and (j) Zn between summation and pseudo total methods of estimating total elemental content from the smelter slag (SS), Inanda soil (Ia), SS treated soils (SS 0, SS7, SS 28, SS 56, and SS 140), electro-winning waste (EW), and the EW treated soils (EW 0, EW 7, EW 28, EW 56, and EW 140). The concentration of these elements extracted by aqua regia after acetic acid, hydroxylammonium chloride and hydrogen peroxide extraction (red bars) was added to the graph to show the contribution of aqua regia on SEP-AR.

The concentration of Co and Cu were higher in BEP-AR compared to SEP-AR for the EW and the EW treated soils. This was also attributed to same mechanism that resulted in high concentration of elements in BEP-$H_2O_2$ compared to SEP-$H_2O_2$. This was also thought to arise from experimental errors when approaching detection limits for these elements in sequential extraction.

## 8.4 Conclusions

The comparison between single and sequential extractions indicated that there is a less degree of comparability between these methods and that comparability is improved when aggressive reagents are compared. Generally, SEP-HAC had higher concentration of elements compared to BEP-HAC. This was attributed to SEP-HAC having the advantage of a continued dissolution and HAC (used after acetic acid) extracting on fresh exposed surfaces. This was also thought to be caused by BEP-HAC having the disadvantage of extracting solution saturation, formation of secondary minerals, and incomplete dissolution of minerals. The extracting solution saturation, formation of secondary minerals, and consequently the incomplete dissolution of minerals were minimal when $H_2O_2$ was applied as single reagents owing it to the aggressive nature of this reagent. Similarly, these disadvantages were minimal with single aqua regia extraction. However, the presence of exposed surfaces in sequential extraction may cause the dissolution of non-target phases, particularly for $H_2O_2$ extraction. Sequential extraction may also transform some elements which may not be released in later extraction steps.

Lastly, the components of the material studied might influence the form of limitation that can occur when single and sequential extractions are compared. This became clear when incomplete dissolution was minimised for the SS and the SS treated soils during $H_2O_2$ extraction but could not be avoided for the EW and the EW treated soils. The main difference between the observed behaviour of these two materials is that the saturation of the extracting solution, which occurs for the SS, could be minimised when $H_2O_2$ was used. Whereas, the incomplete dissolution of thermodynamically stabe minerals in the EW could not be avoided. Hence, the limitation in the comparability between single and sequential extractions can be caused by both the reagent used for extraction and material being extracted.

# CHAPTER 9

# GENERAL DISCUSSION AND CONCLUSIONS

## 9.1 Introduction

The present investigation was conducted in an attempt to assess the suitability of applying the various soil tests within a waste management scenario. It became clear after a review of literature that in order to fully address the question of 'suitability' certain aspects of chemical extraction methods needed to be well understood. These aspects are mainly governed by the characteristics of the material under study. Hence, the present investigation was carried out by comparing commonly used chemical extraction methods with respect to their abilities to extract elements from soil, waste, and/or soil-waste mixtures. The study indicated that the focus should not be on the type of material (i.e. soil, waste, and/or soil-waste mixtures) but rather on the properties of the material being extracted.

The aim of chemical extraction methods is to assess the availability, mobility, and solubility of elements with varying environmental conditions. The results from the extractions are affected by the interaction between the properties of the material being extracted and the extraction conditions, including the extracting reagent. Hence, an approach which takes into account these interactions is proposed and outlined below. This approach should assist in selecting which extraction reagent and what extraction conditions to use for a given material.

## 9.2 Discussion

### 9.2.1 The extraction conditions

The properties of the material being extracted, which need to be considered when deciding on extraction conditions, are mineralogy, pH and pH buffering capacity, soluble salt content, and sorption properties (Figure 9.1). These properties may result in saturation of the extracting solution, incomplete dissolution of minerals, formation of secondary minerals, and readsorption of released elements. These problems can be overcome by using aggressive conditions, chelating agents, buffered extracting reagent,

and high solution:solid ratio (right hand side of Figure 9.1). This is expected to improve the results of extractions.

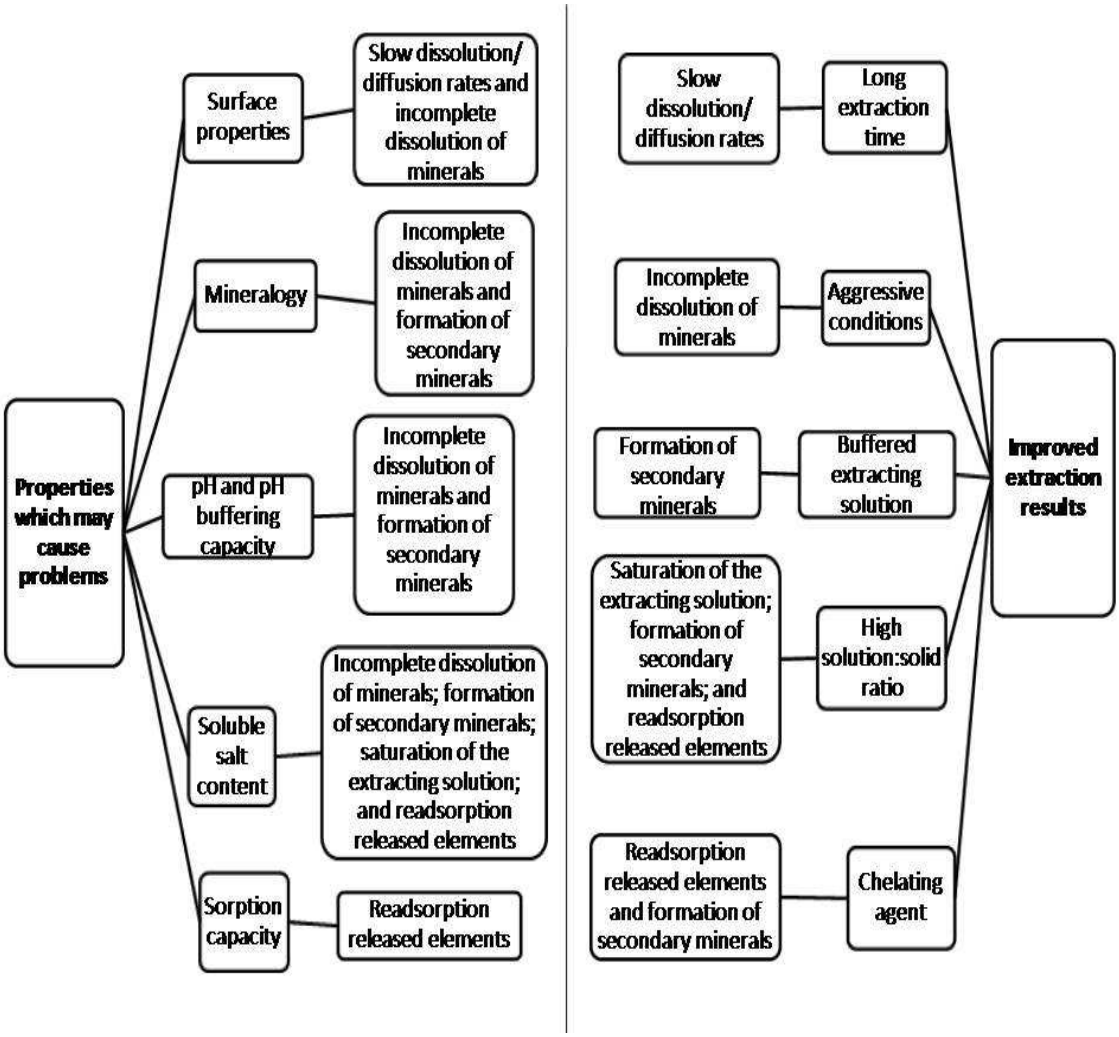



**Figure 9 1** A diagram showing how the extraction results can be improved by selecting extraction conditions that take into account the properties of the material being extracted. The corresponding properties of such materials that may cause problems during extraction and the possible problems that may arise are on the left hand side. The right hand side shows how these possible problems can be minimised, and hence improve extraction results.

The release of Fe and Mn from the EW was limited by the incomplete dissolution of magnetite and jacobsite as well as by the formation of magnetite during HAC

extraction. The incomplete dissolution of magnetite and jacobsite could be minimised by using aggressive conditions such as increased temperatures and aggressive reagents such as oxalic acid. The advantage of oxalic acid, in addition to its ability to dissolve crystalline minerals, is that it could complex Fe and Mn, thus possibly preventing the formation of secondary minerals during the reductive dissolution of the EW.

The advantage of having both the aggressive conditions (and a reagent) and the complexing agent was observed when comparing sequential and single batch extractions. Sequential and single batch extractions were comparable for the S in the SS treated soils when $H_2O_2$ extraction, which combines aggressive conditions and a complexing agent, was used. The complexing agents do not only improve the dissolution of minerals, but also minimise the formation of secondary minerals and the readsorption of released elements by reducing their free ion concentration in solution through ion pair formation. The reduced concentration of elements in solution implies undersaturation of elements with respect to the formation of the secondary minerals and also reduces readsorption of released elements.

The saturation of the extracting solution is often caused by high content of soluble salts, particularly for the EW. This as mentioned, can be minimised by complexing agent and also by using a high solution:solid ratio. Materials having a high content of soluble salts and a high sorption capacity may suffer from the readsorption of elements (such as Ca in the EW) before the release of other elements is complete. Furthermore, high Ca content in the EW resulted in the formation of insoluble calcium sulphate during acetic acid extraction for the EW treated soils. This was attributed to the release of organic acids which compete with the sulphate ions for the ion exchange sites; organic acid would be released when the EW interacted with the Ia soil. This further illustrates the effect of soluble content on the readsorption of released elements and formation of secondary minerals.

The presence of a high soluble salt content could have also delayed the dissolution of minerals. Carbonic acid resulted in mineral dissolution in the Ia soil and the SS. However mineral dissolution did not occur in the EW. The distinguishable difference

between the EW and the other materials was in the soluble salt content. The low soluble salt content could also narrow the gap between the complete release of available (exchangeable and specifically adsorbed) elements and those released due to mineral dissolution. This gap might be increased by using milder or weaker reagents for elements with low soluble salt content.

### 9.9.2 The extracting reagents

The choice of the extracting conditions can be affected by the properties of the material being extracted while the choice of the extracting reagent can be affected by the element(s) of interest. The choice of the extracting reagent is also affected by the fraction of element(s) that need to be assessed.

Oxalic acid, for instance, is aggressive but forms insoluble Ca/Pb oxalates. Hence, if Ca and Pb are the elements of interest, another reagent (such as 0.5 M HAC (in 25% HOAc) at pH of 1.5 and using high temperature) should be used as an alternative to assess the reducible fraction. Hydrogen peroxide and sodium pyrophosphate may also form insoluble Al, Mn, and Fe phosphate minerals. Therefore, when assessing the oxidisable fraction of these elements, NaOCl may be used.

The choice of reagent is also affected by whether or not the reagent will be applied as a single or sequential extraction. Aggressive reagents can result in complete dissolution of minerals when applied as a single extraction, however, these (aggressive reagents) may suffer from lack of selectivity when applied in sequential extraction. Figure 9.2 shows the seesaw relationship between aggressive and weak/mild reagents and also indicates that weak/mild reagents, although selective, may suffer from incomplete dissolution of minerals. This is also important, since the release of some elements is pH dependent and the continued acidity provided in sequential extractions may improve their release.

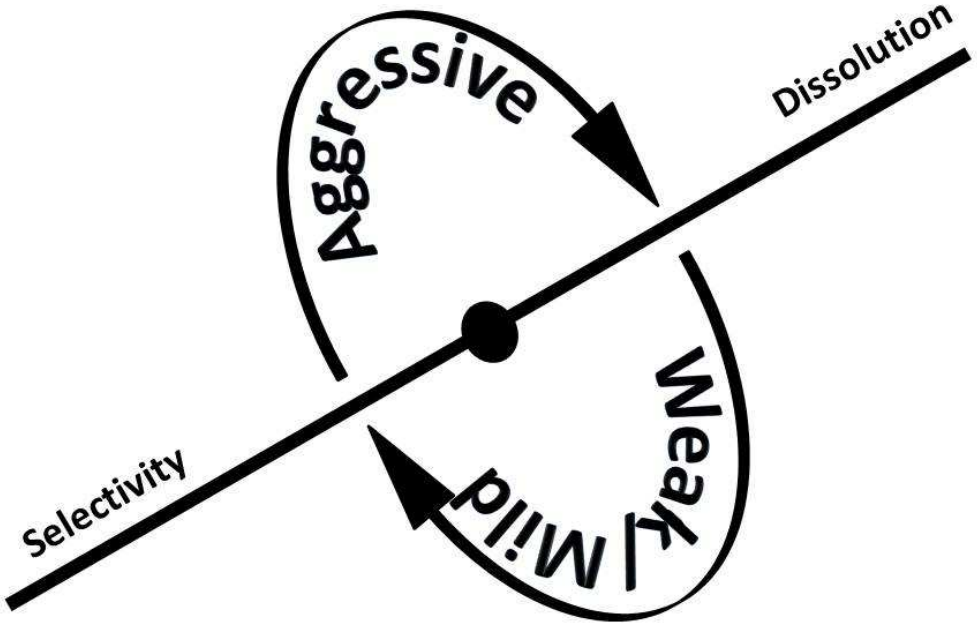



**Figure 9.2** Diagram illustrating the seesaw relationship between weak/mild and aggressive extracting reagents.

When aggressive reagents are applied as sequential extractions they may release elements from non-targeted fractions. Whereas, weak/mild reagents used in batch extractions may result in readsorption of released elements, formation of secondary minerals, and incomplete dissolution of minerals. However, mild reagents may increase the gap between the release of different fractions of elements from one single extraction. This may assist in assessing the time required for a complete release of elements for more mobile fractions. For instance, a reagent weaker than carbonic acid might increase the gap between the release of available (exchangeable and specifically adsorbed) Ca and Mn and the release of the same elements due to mineral dissolution from the SS.

The lack of selectivity when aggressive reagents are used was evident when comparing sequential and single batch extractions. Batch ammonium nitrate and acetic acid extractions released lower concentrations of Al and Fe as compared to the

concentrations of these elements released in sequential extractions. This was attributed to continued dissolution of the amorphous minerals when these reagents were applied in a sequential extraction. This could imply that these reagents may not be selective when applied in a sequential extraction.

## 9.3 Conclusions

Although the approach proposed here may assist in the use of chemical extraction methods, it has limitations. It does not fully account for the release of elements due to continued acidity such as in the SS. Nevertheless, it is proposed that this approach will assist in addressing the question of using soil tests in waste management scenarios.

The above discussion illustrates that the difference between soils, wastes, and waste contaminated soils is property based. Therefore, in an attempt to address the suitability of applying chemical extraction methods in waste management scenarios the above discussion needs to be considered. Based on the discussion above, it was concluded that chemical extraction provide useful information regarding the behaviour of the waste and might be able to predict the release of elements from wastes. However, when chemical extraction methods are used certain modifications need to be made. These modifications include the use of a high solution:solid ratio and an extracting solution which has high complexing ability. Finally, when chemical extraction methods are applied to wastes, the effects of the waste properties on the results of extraction need to be well understood.

## 9.4 Recommendations

The following recommendations might improve the extractability of elements and the use chemical extraction methods. These recommendations are:

- An investigation assessing the release of elements from different fractions using alternative reagents for a wide range of materials with different properties. This may assist in evaluating the usefulness of the approach proposed here. It will also assist in categorising effective extraction reagents with their corresponding material properties,

- Further investigation of the effect of extraction time on chemical extraction methods. This investigation should assess times investigated here and times which are less than 16 hours so that beginning of readsorption may be monitored. Such investigation should assess other reagents such as acetic acid which release available elements but can cause dissolution of minerals, and
- An investigation on the use of higher solution:solild ratio in minimising readsorption of released elements.

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# APPENDICES

**Appendix 3.1** The methods used in charecterising the electro-winning waste, smelter slag, and A horizon of Inanda soil form

Physical and chemical characterisation

Organic carbon (OC) was determined by potassium dichromate oxidation and determined titrimetrically on < 0.5 mm material (Walkley, 1947). Electrical conductivity and pH were measured using a solid:solution ratio of 1:2.5 (10 g solid:25 mL solution) in distilled water. The pH was also measured in 1 M KCl using the same soil:solution ratio as for the water extract. Extractable cations and cation exchange capacity were measured by saturating with $Sr^{2+}$ and subsequent replacement with $NH^{4+}$ (Hughes and Girdlestone, 1994). Total elemental concentrations were measured by X-ray fluorescence spectrometry (XRF, Geology Department, University of KwaZulu-Natal, Durban).

Nitrate and ammonia were extracted with 2M KCl (Maynard and Kalra, 1993) and solution concentrations determined colorimetrically using a TRAACS 2000 continuous flow auto analyser. This could not be performed on the EW due to chemical interferences. Thus, total $NH^{4+}$ - N was determined by direct distillation using a Gerhardt Vapodest 1 distillation unit.

Plant available phosphorus was estimated by extracting with AMBIC (ammonium bicarbonate) solution and P was determined colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990) on a Varian Cary 1E UV-Visible spectrophotometer (UV-Vis). Exchangeable acidity and exchangeable Al were measured according to Sims (1996), with Al being measured by atomic absorption spectrophotometry (AAS, Varian SpectraAA-200). Calcium carbonate equivalence (CCE) was measured according to Jackson (1958).

Saturated paste extracts (Soil Salinity Laboratory Staff, 1954) were analysed for Al, Ba, Ca Cd, Co, Cr, Cu, Fe, hg, K, Mg, Mn, Na, Ni, P, Pb, S, Se, Sr, V, and Zn by ICP

(Liberty X150). Nitrogen in the solution was determined using ammonia probe. The EC of the extracts was also determined.

Mineralogy

X-ray diffraction analysis on random powders was carried out on a Philips PW1050 diffractometer using monochromated Co Kα radiation (from $3^o$ to $75^o$ 2θ) with a scanning step of $0.02^o$ at $1^o$ per minute counting interval. The diffraction data were captured by a Sietronics 122D automated micro-processor attached to the X-ray diffractometer. The samples were then qualitatively analysed to determine major mineralogical components.

The materials were also examined by electron microscopy (ESEM) and semi quantitative chemical composition determined by energy dispersive X-ray (EDX) analysis (Centre for Electron Microscopy, UKZN, Pietermaritzburg).

Dissolution investigation

The dissolution of selected elements from the EW and SS (both <0.5 mm) were determined in solutions over a wide pH range. Thirty mL of solution (at pH's of 0.5, 1, 3, 5, 7, 9, 11; adjusted using HCl or NaOH) were added to 6 g of waste material, shaken on an end-over-end shaker for 16 h, centrifuged at 3000 r.p.m. and filtered. The pH of the final extract was measured and concentrations of Ca, S, Mn, Fe, Pb, Al and Mg were determined using ICP (Liberty X150). Silicon in solution was determined by the molybdate blue method (Fox *et al.*, 1969). The dissolution was conducted in duplicates.

Adsorption studies

Phosphorus adsorption isotherms were determined for the SS and EW. Twenty-five mL of a range of P solutions (0, 2, 4, 8, 16 and 32, 50, 100, 250, 500 and 1000 mg P $L^{-1}$) were added in a 0.01M $CaCl_2$ matrix to 1 g of material. The mixtures were shaken on a reciprocating shaker for 18 h, centrifuged for a five minutes and the supernatant analysed for P colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990).

Metal adsorption isotherms were also determined for the wastes. Twenty-five mL of a range of either, Pb, Zn, Cu or Ni solutions were added to 1 g of the wastes and the mixtures were shaken for 24 hrs. The extracts were analysed for the respective metals by AAS.

**Appendix 3.2** The expected behaviour of magnetite and jacobsite with varying environmental conditions

Magnetite has low solubility in aqueous solutions (Lindsay, 1979; Essene and Peacor, 1983). It can be solubilised under reducing conditions where Fe (III) is reduced to Fe (II) (Lindsay, 1979; Essene and Peacor, 1983; Klemm, 2000). Magnetite also dissolves at low pH. It has also been reported to be dissolved by a number of reagents such as HCl, oxalic acid, hydroxlyammonium chloride, ascorbic acid, and EDTA (Chao and Zhou, 1983; Gu et al., 1994; Manjanna et al., 2001; Al-Mayouf, 2003; Bauer and Blodau, 2006; Laforest and Ducheshe, 2006; Perdersen et al., 2006). Oxalic acid has been reported to dissolve about 25-35 % of magnetite (Chao and Zhou, 1983). The results from Chao and Zhou (1983) suggest that the dissolution of magnetite at low pH, or in the presence of organic acids, or under reducing conditions is not necessarily complete. This incomplete dissolution of magnetite has implications for the use of reducing agents at low pH in sequential extractions.

There is limited information on the dissolution of jacobsite, though the possible dissolution mechanism for jacobsite can be deduced from its constituents. Jacobsite consists mainly of Fe and Mn. These two metals may be present in either the 2+ or 3+ oxidation states in both tetrahedral and octahedral coordination. There are four main forms in which jacobsite exist. The first one consist of Mn (II) and Fe (III) in jacobsite structure in a ratio of 1:2 (Villinski *et al.*, 2001; Hu *et al.*, 2005). The second form has Mn (III), Fe (II) and Fe (III) in a ratio of 1:1:1 (Bühn *et al.*, 1995; Villinski *et al.*, 2001). The third form of jacobsite has both Mn and Fe in the 2+ and 3+ oxidation states (Ponnamperuma *et al.*, 1969; Gabal and Ata-Allah, 2004; Hu *et al.*, 2005). In the fourth form Mn is present as both Mn (III) and Mn (II) and Fe is present as Fe (III) (Osawa *et al.*, 1992; Bühn *et al.*, 1995). The existence of Mn and Fe in both 3+ and 2+ oxidation states suggests that jacobsite could dissolve under both reducing and oxidising conditions depending on the oxidation states present.

Jacobsite, as indicated in equation 3.2, has low solubility (log K = -1.24) and is expected to dissolves at low pH and under reducing conditions (Figure 3.3). The

products of reductive jacobsite dissolution would be Mn (II) and Fe (II). Released Fe (II) in solution can be easily oxidised to Fe (III) under aerobic conditions above pH 4 or if jacobsite which contains Mn (III) is present. Manganese (III) is both a strong oxidising and reducing agent and can disproportionate to form Mn (II) and $MnO_2$ (Bartlett, 1986; Greenwood and Earnshaw, 1984). Reduction of both Mn (III) and $MnO_2$ to Mn (II) by Fe (II) can occur (Bartlett, 1986; Villinski *et al.*, 2001). However, unlike Fe (II), Mn (II) is not readily oxidised (Greenwood and Earnshaw, 1984). Iron (II) will then get oxidised to Fe (III) and can precipitate out as magnetite. This may result in non-stoichiometric release of Fe and Mn from jacobsite, where the concentration of released Mn is higher than that of Fe.

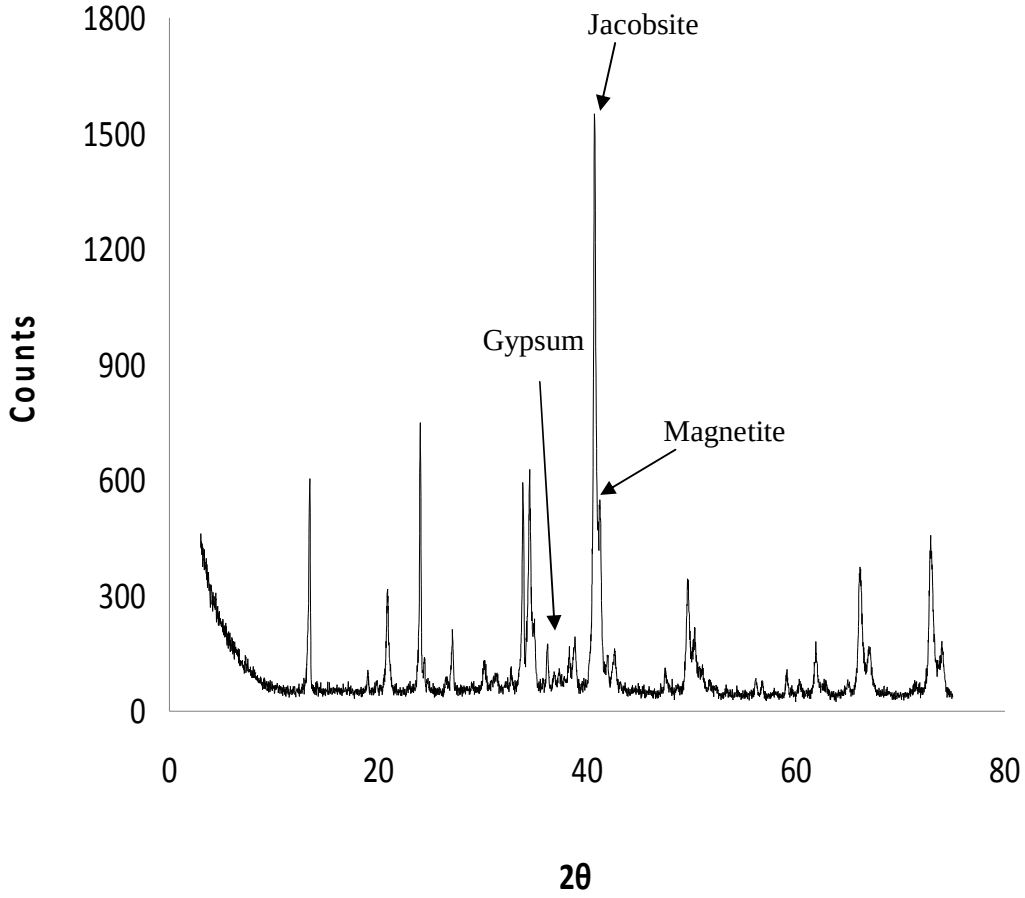
The strong oxidising capacity of Mn (III) has implications for the application of the EW on materials that dissolve under oxidising conditions. Organic matter and sulphides minerals dissolve under oxidising conditions. The disposal of the EW on soils that has high organic matter content or sulphide minerals may results in the dissolution of these materials if jacobsite in the EW contains Mn (III). Titshall (2007) found high release of Mn in the presence of organic matter. This may, although not conclusive, suggest that jacobsite in the EW contains Mn (III).

Jacobsite may dissolve under oxidising conditions where Mn could be oxidised to Mn (III), $MnO_2$, and possibly Mn (VII) and Fe to Fe (III). The oxidised Mn (III) will easily disproportionate to Mn (II) and $MnO_2$, and Mn (II) will be oxidised by $MnO_2$ through the autocatalytic oxidation to either Mn (III) oxides or MnOOH (Bartlett, 1986). Manganese (II) can also be oxidised by hydrogen peroxide and Cr (VI) to $MnO_2$ (Greenwood and Earnshaw, 1984; Hu *et al.*, 2005). However, hydrogen peroxide can reduce $MnO_2$ to Mn (II) at low pH or in the presence of a chelating ligand and Fe (III) to Fe (II) at alkaline pH (Bartlett, 1986; Greenwood and Earnshaw, 1984). Possible effects of oxidising conditions, particularly the presence of hydrogen peroxide, on jacobsite are not clear but it is predicted that hydrogen peroxide will dissolve jacobsite.

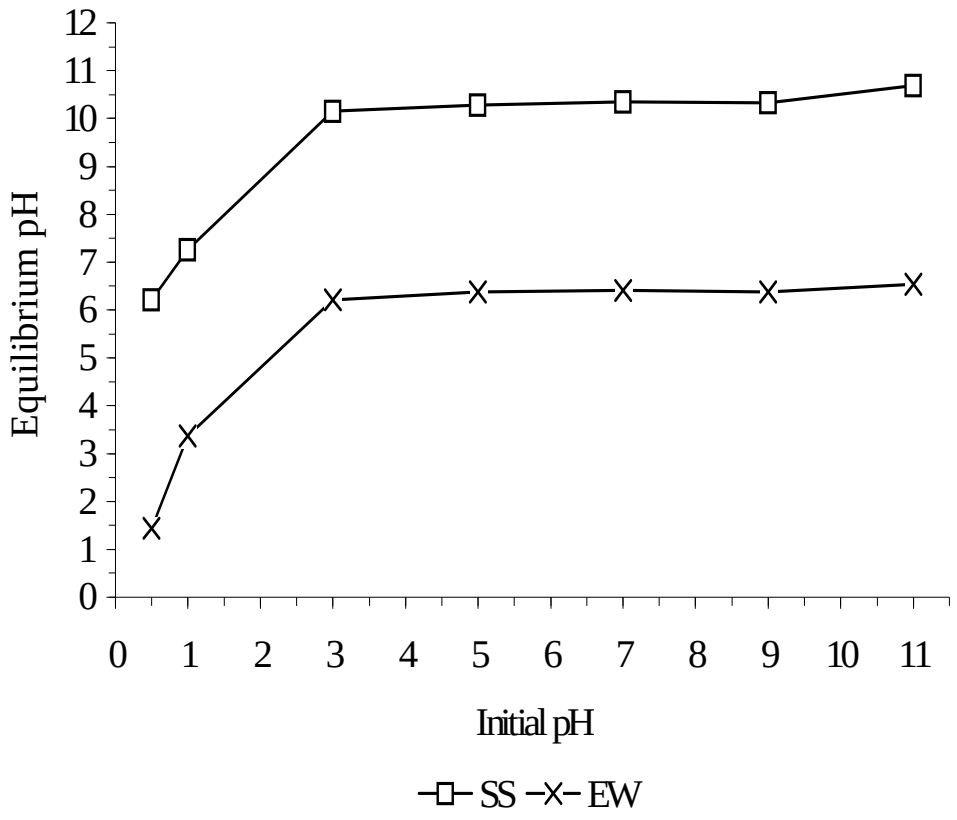
The consequences of oxidising conditions on jacobsite are dependent on the oxidation states of Fe and Mn. If jacobsite contains Mn (II) and Fe (III) then Mn would be

oxidised to either Mn (IV), which is more likely, or to Mn (III). However, if Fe is in a reduced state then Fe (II) will oxidised to Fe (III). Transformation of Fe (II) to Fe (III) can also cause reduction of Mn (III) and Mn (IV) to Mn (II). Whether the released Mn (II) will remain on solution or not depends on the availability of oxidising agent. This suggests that Mn would be released in the fractionation studies when both the reducing and oxidising reagents are used.

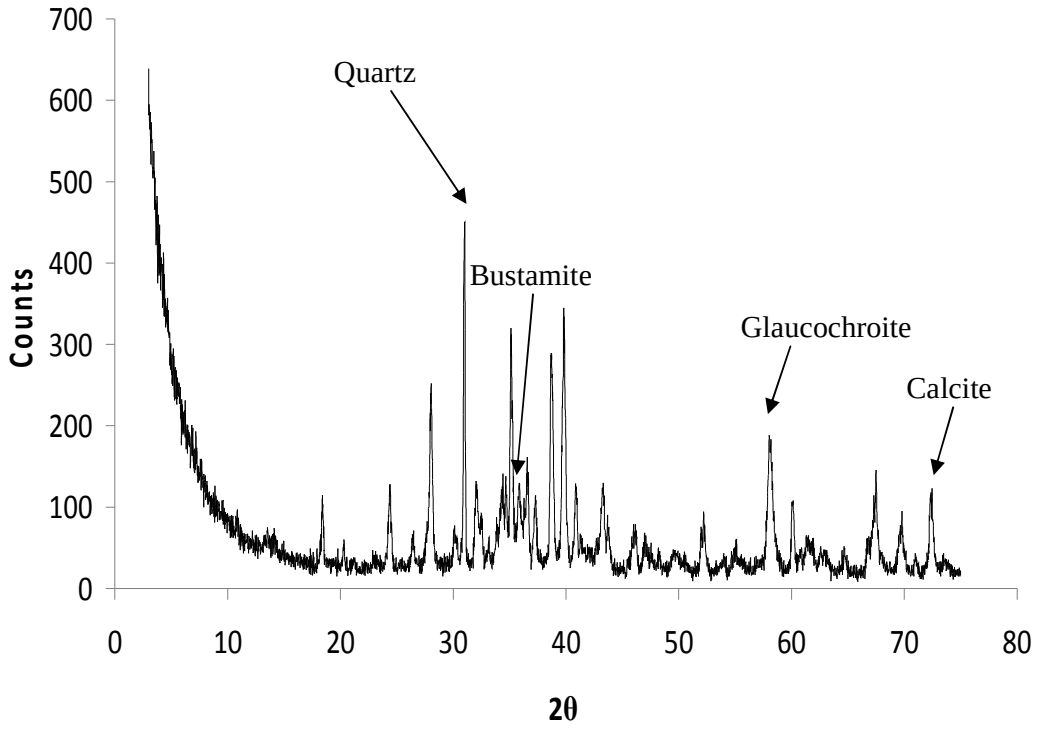
**Appendix 3.3** The X-ray diffraction pattern for random orientated powder sample the electro-winning waste. The dominant peaks ($I/I_i$ = 100) of the minerals are indicated



**Appendix 3.4** Equilibrium solution pH of the smelter slag (SS) and electro-winning waste (EW) treated with solutions of different initial pH (Titshall, 2007)



**Appendix 3.5** The X-ray diffraction pattern for random orientated powder sample the smelter slag. The dominant peaks ($I/I_i$ = 100) of the minerals are indicated



**Appendix 3.6** The expected behaviour of olivine (gluacochroite) with varying environmental conditions

Olivines have low stability and are readily soluble (log K = 37.82) in aqueous solution over geological time (Huang, 1989; Jonckbloedt, 1998). It has also been reported that olivines dissolve readily at low pH or in the presence of organic acids (Grandstaff, 1978; Siegel and Pfannkuch, 1984; Velbel, 1993; Jonckbloedt, 1998; Welch and Banfield, 2002; Hänchen *et al.*, 2006). The dissolution of olivines is often accompanied by an increase in pH which indicates the consumption of protons during dissolution (Siegel and Pfannkuch, 1984; Velbel, 1993; Jonckbloedt, 1998; Hänchen *et al.*, 2006).

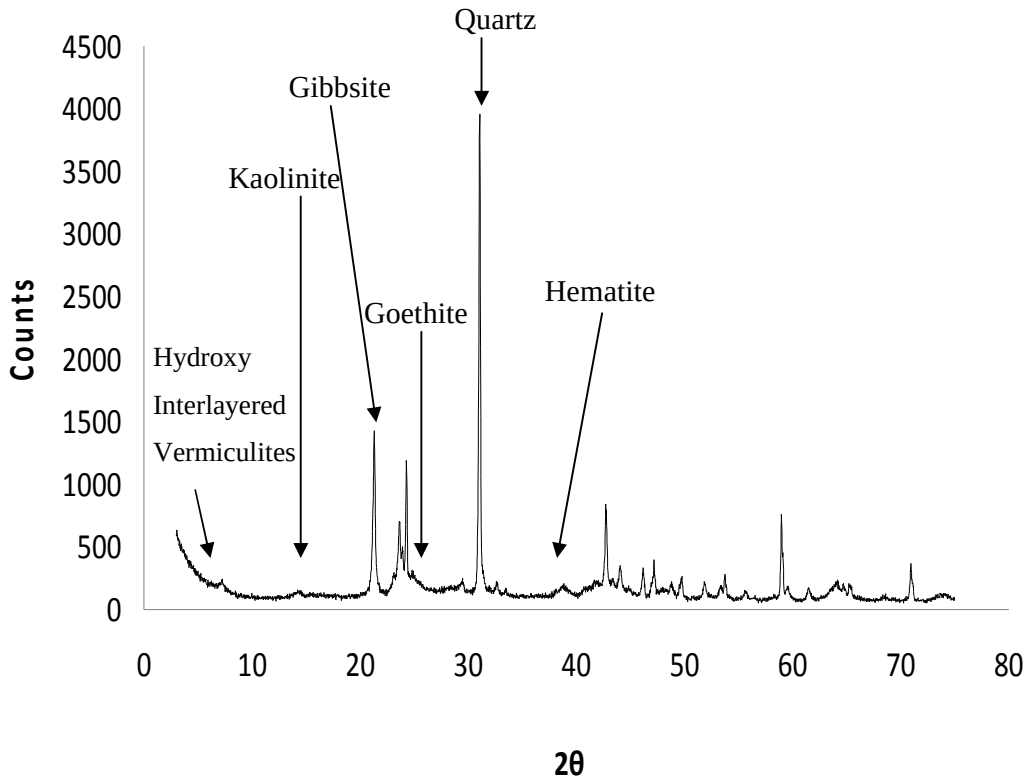
The dissolution of glaucochroite will result in the release of Ca, Mn, and Si into solution. However, the increase in the concentration of Si in solution may result in the secondary formation of Si polymers which will reduce the concentration of Si in solution. Jonckbloedt (1998) indicated that Si polymerises as the solution concentration of Si exceeds 100 mg $L^{-1}$. Titshall (2007) found, and confirmed (using XRD and electron microscope) the formation of 'silica-gel' at high Si concentration. The newly formed 'silica-gel' can coat the surfaces of glaucochroite and result in incomplete dissolution

The incomplete dissolution of glaucochroite due surface coatings is favoured by high pH and supersaturation of the solution with respect to secondary minerals. The precipitation of secondary minerals has been reported to have an inhibitory effect on the dissolution of silicate minerals (Siegel and Pfannkuch, 1984; Drever and Stillings, 1997; Gerard *et al.*, 2003; Hänchen *et al.*, 2006). Furthermore, these authors have also documented a decrease in dissolution rate when the solution approached saturation with respect to secondary minerals (such as brucite and Fe hydroxides) even though secondary minerals had not yet been precipitated (Siegel and Pfannkuch, 1984; Drever and Stillings, 1997; Hänchen *et al.*, 2006).

The formation of secondary minerals can be minimised in the presence of chelating agents and organic acids which will remove the free ion from solution thus promoting

the reaction to shift to the right hand side and dissolution of minerals (Drever and Stillings (1997). Thus when assessing the suitability of the various ‘soil tests’, care will have to be taken, to account for the development of supersaturated solution with subsequent precipitation of secondary minerals. Furthermore, consideration needs to be given to the use of organic acids and chelating agents which can overcome these problems and also enhance the rate of extraction.

**Appendix 3.7** The X-ray diffraction pattern for random orientated powder sample the A horizon of Inanda soil form. The dominant peaks ($I/I_i$ = 100) of the minerals are indicated



**Appendix 3.8** The expected behaviour of the Inanda soil with varying environmental conditions

The Ia soil has high OC (9.60 g 100g-1) content and is predominantly composed of hydroxyl-interlayered vermiculites (HIV), kaolinite, hematite, goethite, quartz, and gibbsite with quartz and gibbsite being dominant minerals. Kaolinite, hematite, goethite, and gibbsite have been reported to dissolve at low pH and in the presence of organic acids (Gu et al., 1994; Chorover and Sposito, 1995; Drever and Stillings, 1997; Bauer and Blodau, 2006; Cama and Ganor, 2006; Pedersen et al., 2006). In contrast, phosphate may inhibit the dissolution of oxides (Stone and Morgan 1984).

Sorption of heavy metals and other elements on the oxide minerals is well documented (Chao, 1972; Chao and Zhou, 1983; van Herck and Vandecasteele, 2001; Neaman *et al.*, 2004a; Bauer and Blodau, 2006; Pedersen *et al.*, 2006; Silveira *et al.*, 2006). The soils which contain these oxides can potentially be used for land application of wastes since heavy metals will be adsorbed on the oxides. However, the dissolution of these minerals will cause the release of adsorbed elements. Furthermore, the high sorption capacity of the oxides creates a problem of readsorption of released elements during extraction (Raksasataya *et al.*, 1996).

The presence of oxide minerals and high OC content of the Ia soil suggests that the Ia soil has a potential to immobilise heavy metals. Organic matter, like oxide minerals, has high sorption capacity for heavy metals. Organic matter also has an additive effect to the adsorption of heavy metals by the oxide minerals. Bradl (2004) reported an increase in the adsorption of Cr (III) on Fe-Mn oxides when organic matter content was increased. However, the retention of Cr (III) could be the results of organic matter forming strong complexes with Cr (III). This provides an example of conflicting reports in the literature regarding the phases that are primarily responsible for sorption of heavy metals when both organic matter and oxide minerals are present.

Some authors have indicated that adsorption is dominated by organic matter when both organic matter and oxide minerals are present (Schnitzer, 1978; Tessier *et al.*, 1996; Lin

and Chen, 1998; Liu *et al.*, 2007). In most of these studies adsorption was studied on a material before and after $H_2O_2$ extraction which is expected to dissolve organic matter. However, $H_2O_2$ extraction may partially dissolved oxide minerals thus decreasing the number of sorption sites. These authors found that removal of organic matter decreased the capacity of the soil to adsorb heavy metals (Schnitzer, 1978; Tessier *et al.*, 1996; Lin and Chen, 1998; Liu *et al.*, 2007). Conversely, the removal of oxide minerals (by leaving organic matter intact) was found to have little effect on the adsorption of heavy metals.

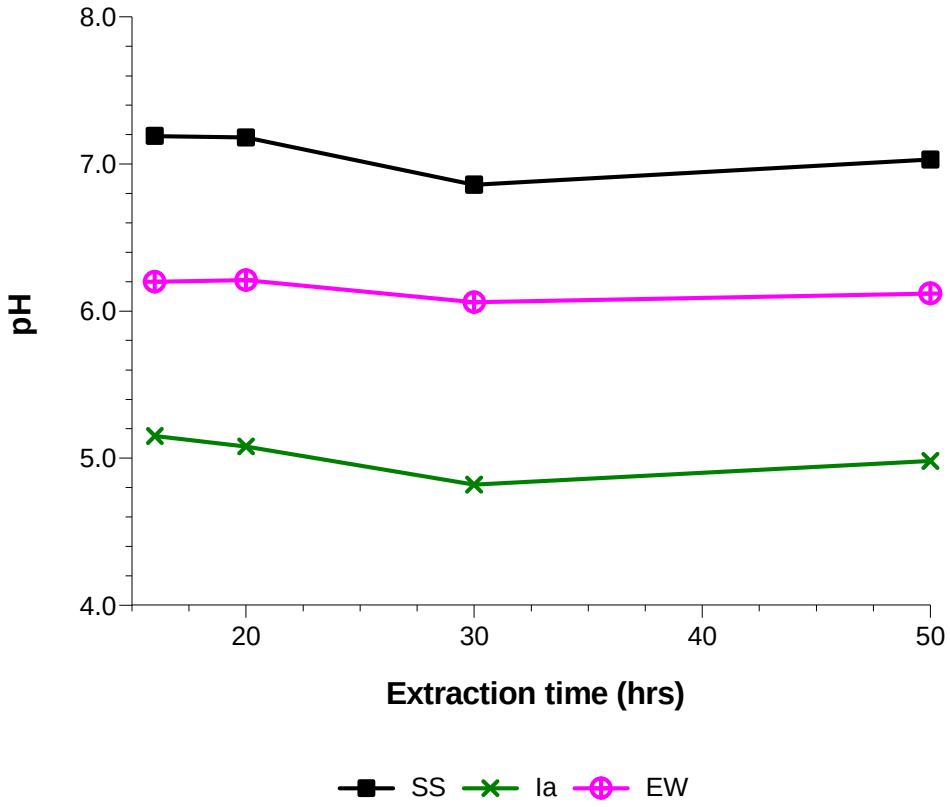
On the other hand, several authors have reported that the adsorption of heavy metals on soil was dominated by oxide minerals over organic matter (Dong *et al.*, 2000; Dong *et al.*, 2002; Bradl, 2004). The removal of oxide minerals resulted in low adsorption of heavy metals while the removal organic matter had minimal effect on the sorption of heavy metals. There is no clear reason for the contradiction reported in the literature. However, Tate (1987) reported that oxide minerals may be important for the long term adsorption of heavy metals where organic matter was responsible for the initial adsorption.

The adsorption of heavy metals on oxide minerals and organic matter has implications for sequential extraction studies. Elements released from a less aggressive reagent may be readsorbed on the oxide minerals and organic matter which will results in their redistribution. The redistribution of released elements may decrease their solubility. Secondly the discrepancies in literature could also be indicating that the reagents used to dissolve certain minerals in sequential extractions are not specific (i.e. they dissolve non-targeted phases).

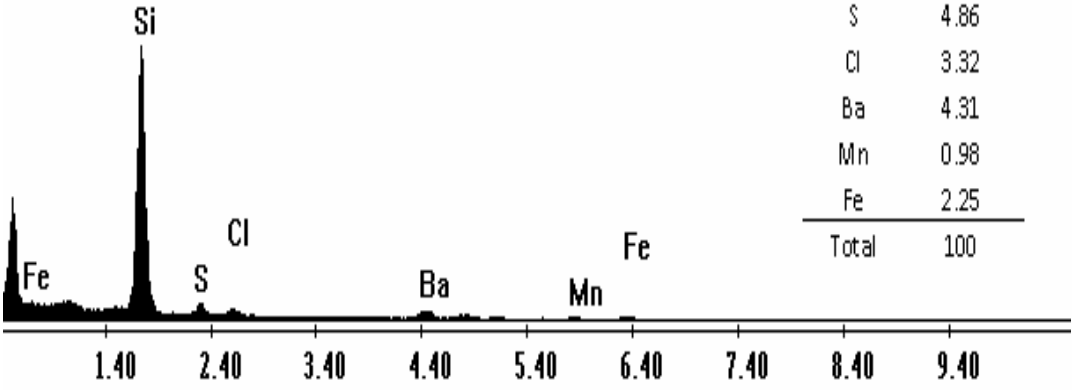
**Appendix 4. 1** The lower limits of detection (LoD) for the elements that were analysed with ICP-OES. The LoD for an element is the concentration that corresponds to the intensity obtained from adding 3*standard deviation (of the intensity of the lowest calibration standard used) to the intercept of the calibration curve

| **Element** | **LoD (mg/L)** |
|---|---|
| Al | 0.245 |
| As | 0.165 |
| Ba | 0.137 |
| Ca | 2.411 |
| Cd | 0.147 |
| Co | 0.134 |
| Cu | 0.174 |
| Cr | 0.012 |
| Fe | 0.308 |
| K | 0.521 |
| Mg | 0.750 |
| Mn | 1.339 |
| Na | 0.166 |
| Ni | 0.116 |
| Pb | 0.079 |
| S | 0.739 |
| Se | 0.122 |
| Sr | 0.031 |
| V | 0.008 |
| Zn | 0.340 |
| Mo | 0.010 |
| Si | 0.031 |

**Appendix 4. 2** The changes in pH of carbonated water with extraction time for smelter slag (SS), Inanda soil (Ia), and electro-winning waste (EW)

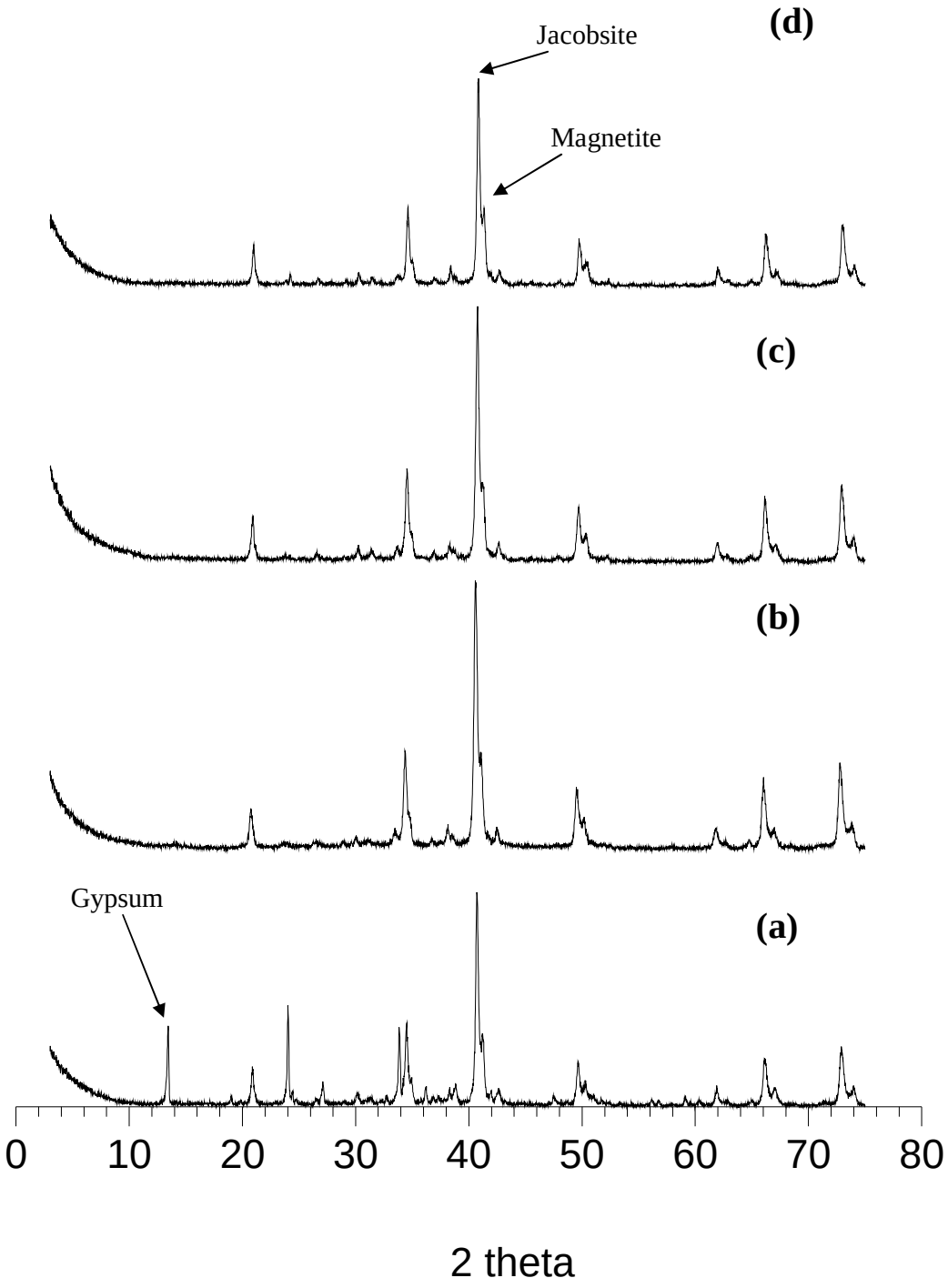


**Appendix 5. 1** A typical EDX trace and the quantification of the elements in the electro-winning waste after acetic acid, hydroxylammonium chloride, hydrogen peroxide, aqua regia extraction indicating that most of Fe and Mn were removed after aqua regia digestion

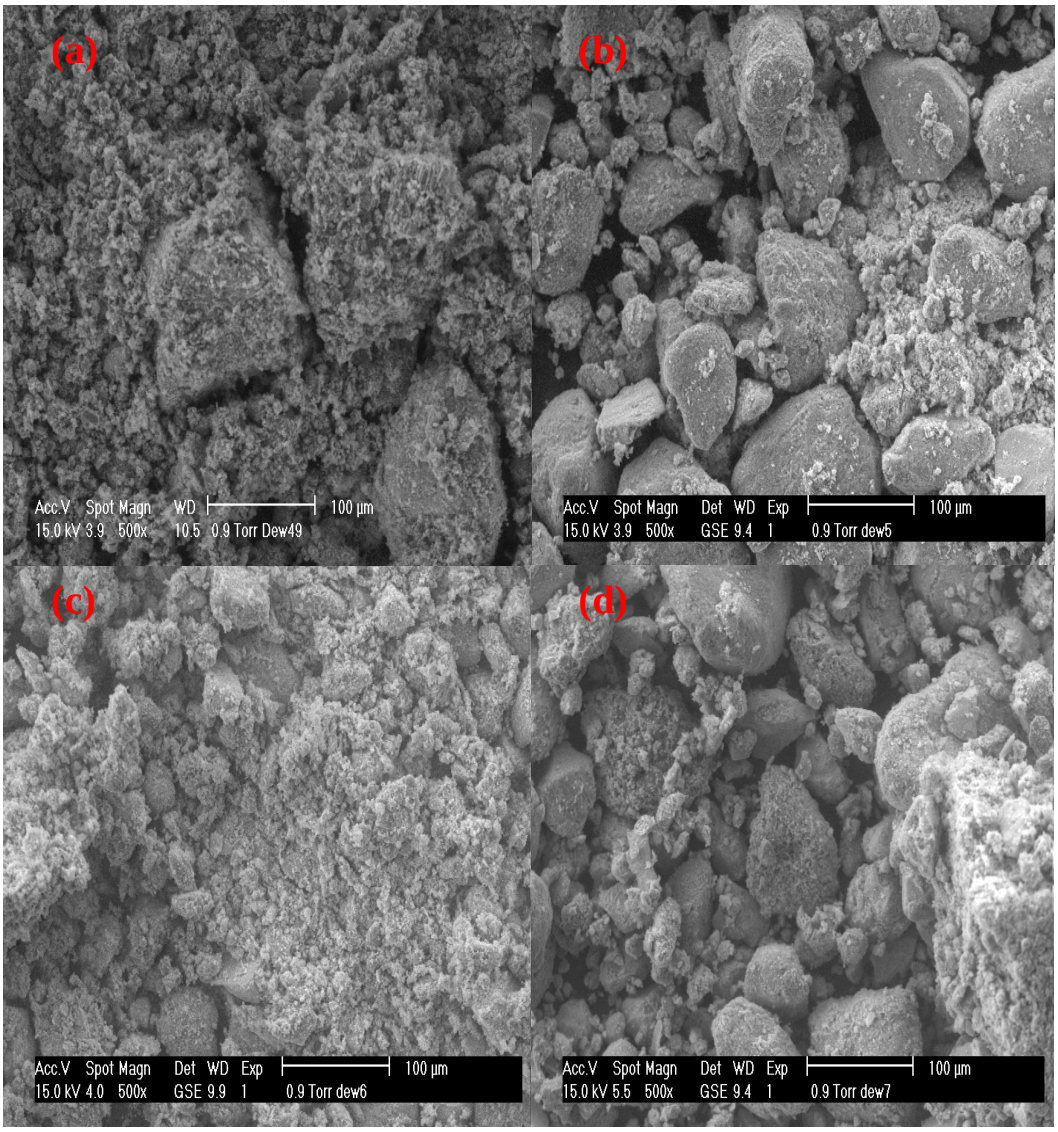



| Element | Weight (%) |
|---|---|
| Si | 84.28 |
| S | 4.86 |
| Cl | 3.32 |
| Ba | 4.31 |
| Mn | 0.98 |
| Fe | 2.25 |
| Total | 100 |

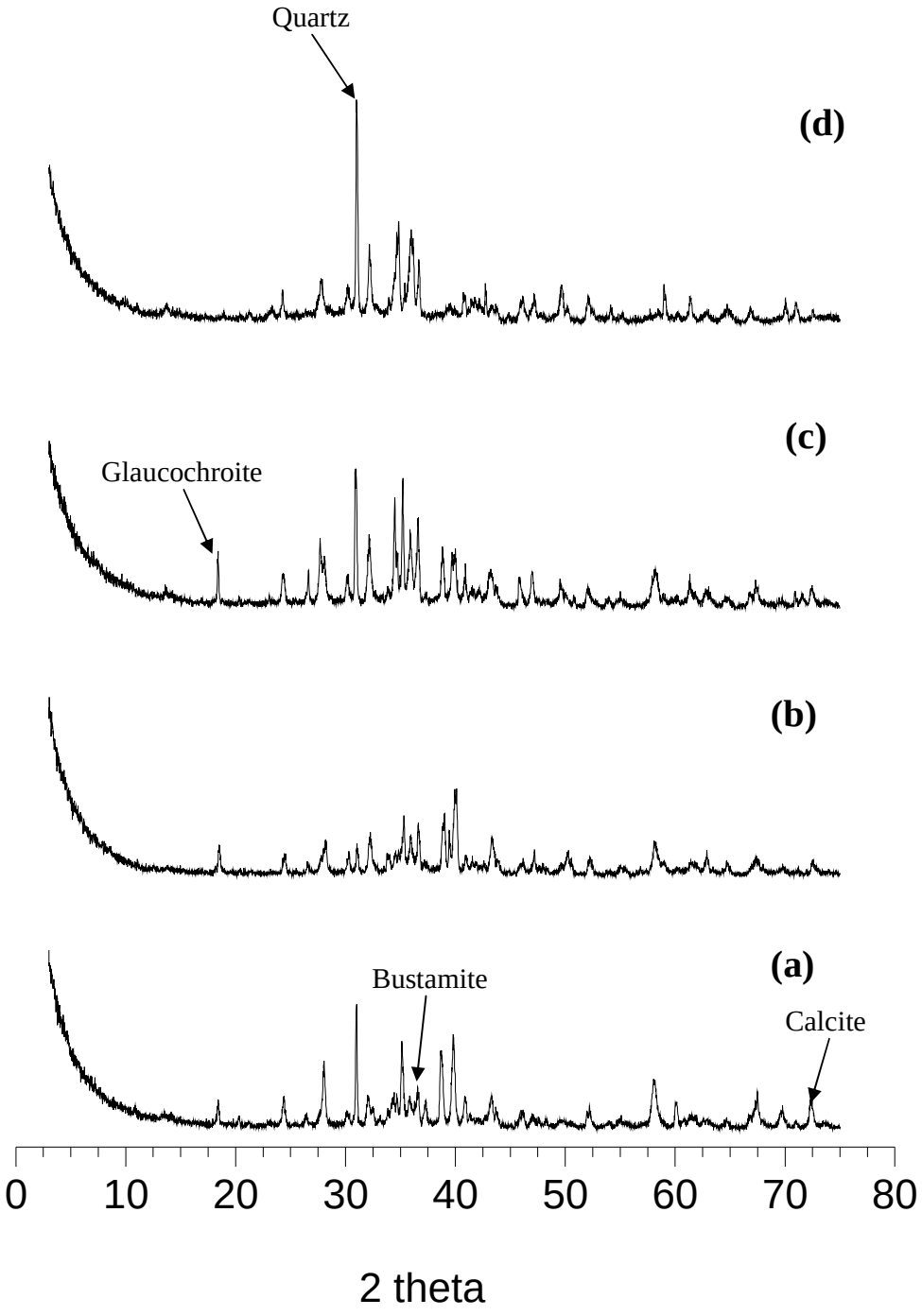
**Appendix 5. 2** The X-ray diffraction patterns for the random orientated powder samples of the electro-winning waste (a) before extraction and after (b) acetic acid, (c) hydroxylammonium chloride, and (d) hydrogen peroxide extraction



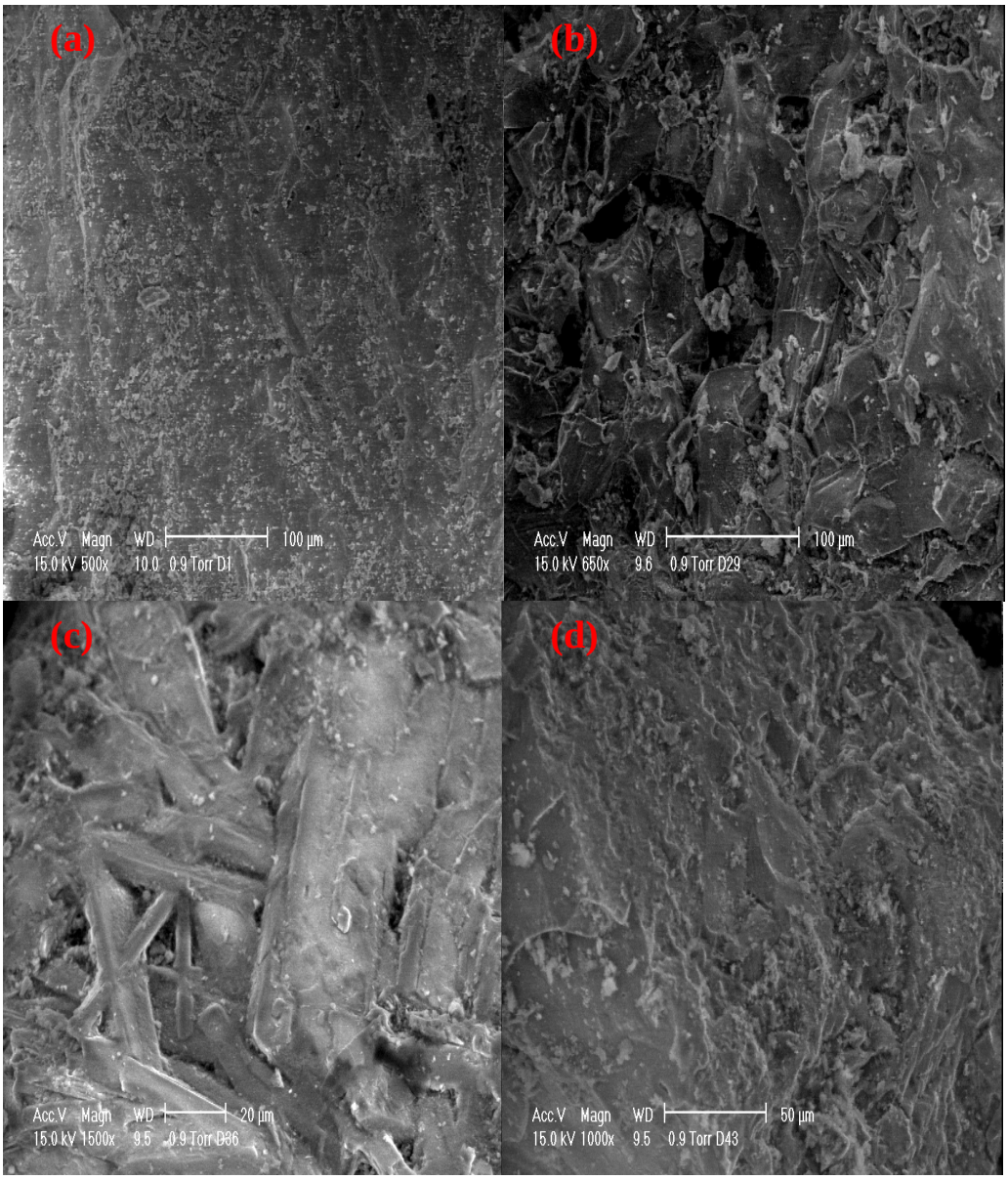
**Appendix 5. 3** The electron microscope picture of the surface properties of the electro-winning waste (a) before extraction and the changes in surface properties after (b) acetic acid, (c) hydroxylammonium chloride, and (d) hydrogen peroxide extraction



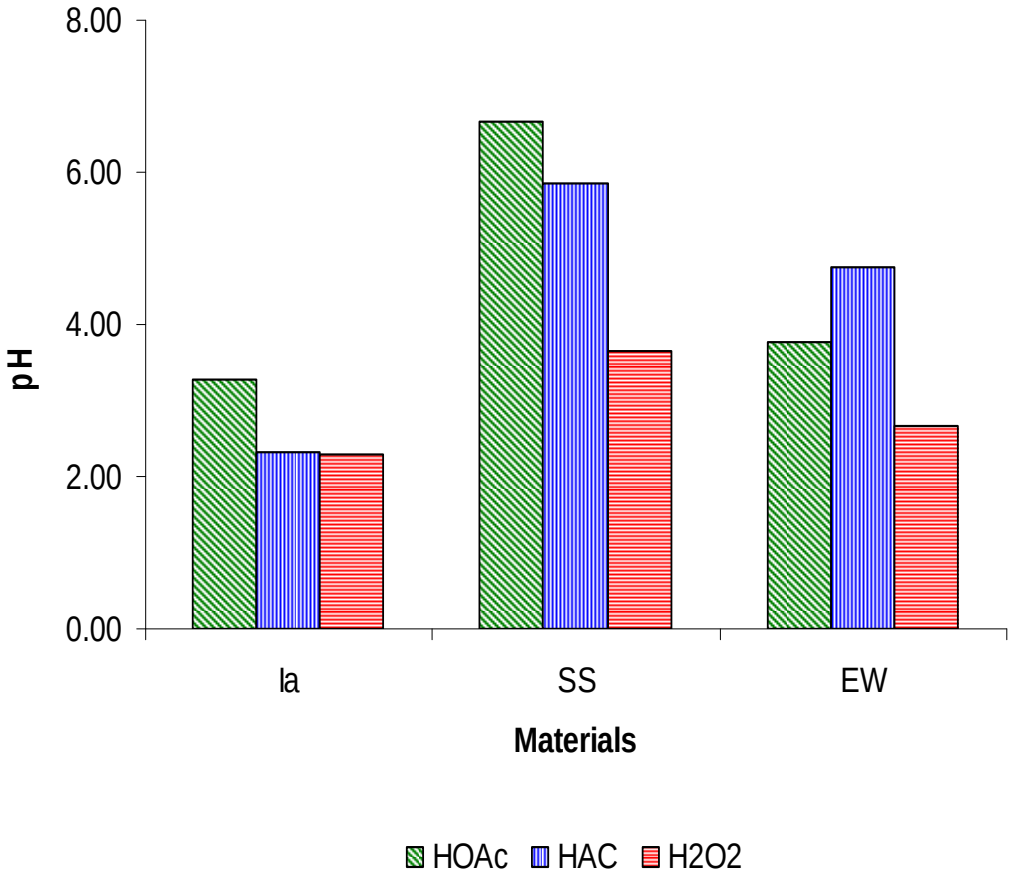
**Appendix 5. 4** The X-ray diffraction patterns for the random orientated powder samples of the smelter slag (a) before extraction and after (b) acetic acid, (c) hydroxylammonium chloride, and (d) hydrogen peroxide extraction



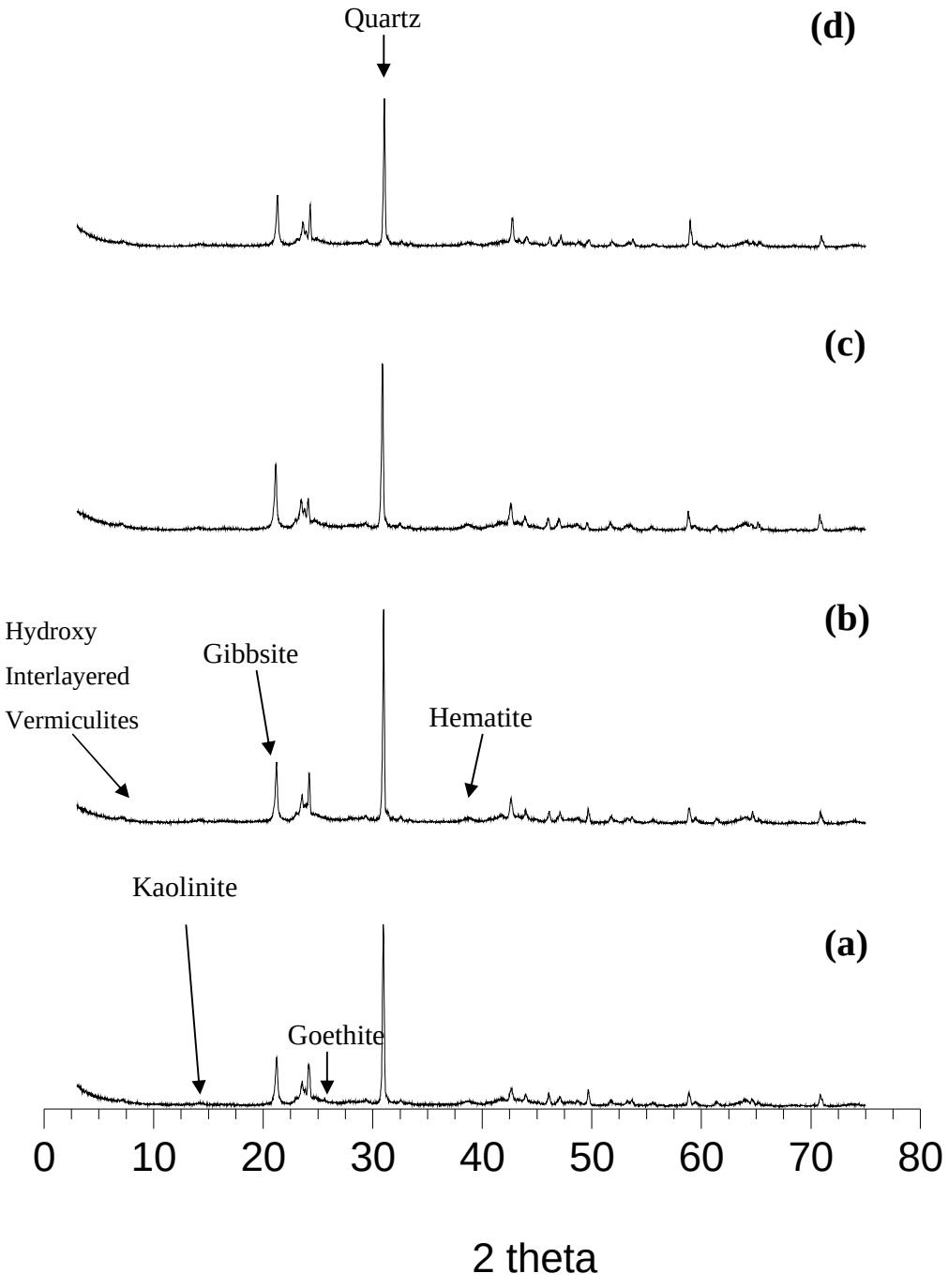
**Appendix 5. 5** The electron microscope picture of the surface properties of the smelter slag (a) before extraction and the changes in surface properties after (b) acetic acid, (c) hydroxylammonium chloride, and (d) hydrogen peroxide extraction



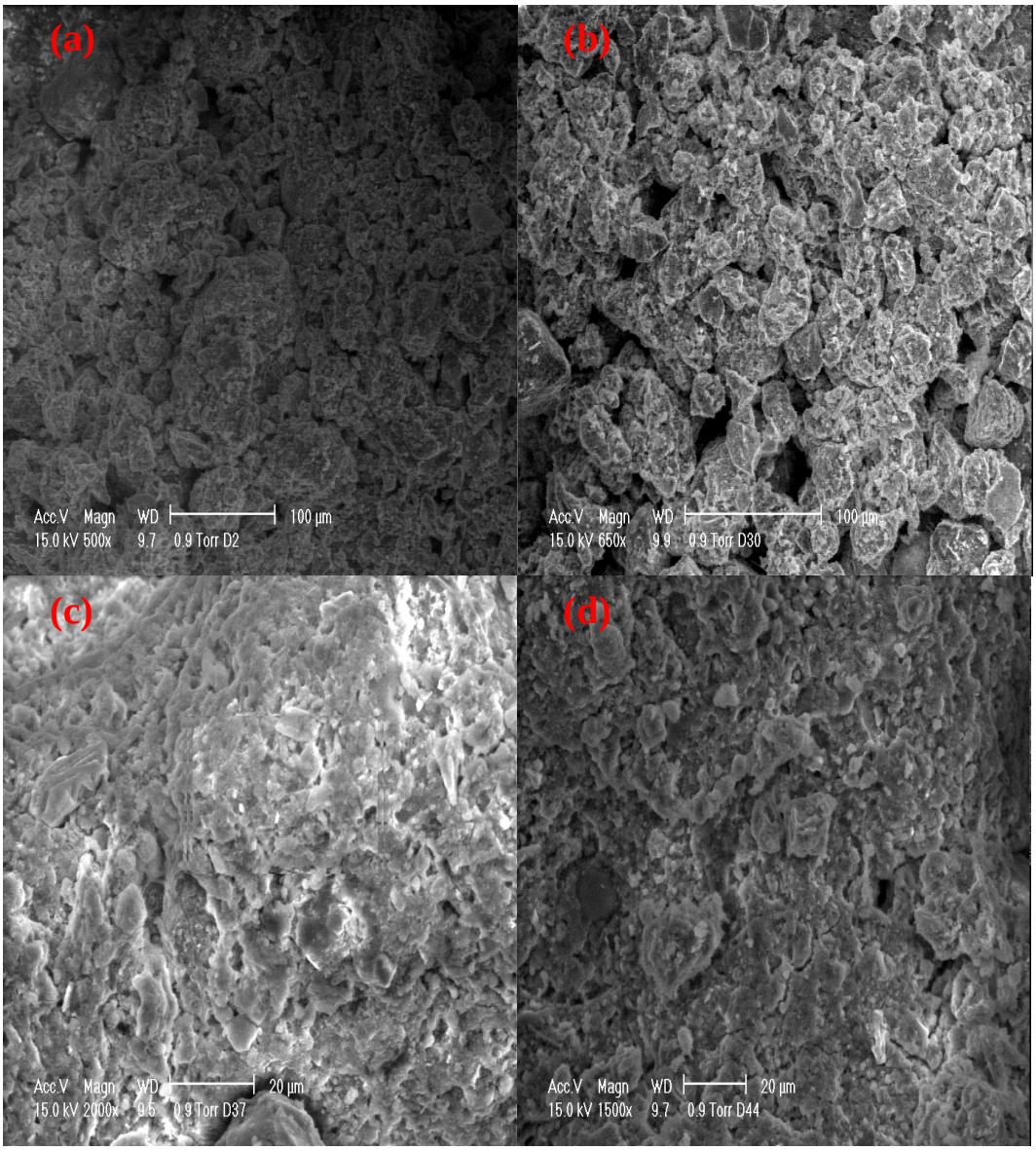
**Appendix 5. 6** The final extraction pH of the A horizon of the Inanda soil form (Ia), smelter slag (SS), and the electro-winning waste (EW) after acetic acid (HOAc), hydroxylammonium chloride (HAC), and hydrogen peroxide ($H_2O_2$) extraction



**Appendix 5. 7** The X-ray diffraction patterns for the random orientated powder samples of the A horizon of Inanda soil form (a) before extraction and after (b) acetic acid, (c) hydroxylammonium chloride, and (d) hydrogen peroxide extraction



**Appendix 5. 8** The electron microscope picture of the surface properties of the A horizon of the Inanda soil form (a) before extraction and the changes in surface properties after (b) acetic acid, (c) hydroxylammonium chloride, and (d) hydrogen peroxide extraction



**Appendix 7. 1** A comparison between sequential (SEP) and batch (BEP) extraction final pH for the exchangeable (EX) and acid-soluble (AS) fractions

| Material | EX | | AS | |
|---|---|---|---|---|
| | **BEP** | **SEP** | **BEP** | **SEP** |
| **Ia** | 4.30 | 4.55 | 3.25 | 3.38 |
| **SS 0** | 5.71 | 6.02 | 4.36 | 4.31 |
| **SS 7** | 5.87 | 6.24 | 4.20 | 4.18 |
| **SS 28** | 6.69 | 6.68 | 4.24 | 4.26 |
| **SS 56** | 6.82 | 6.83 | 4.32 | 4.24 |
| **SS 140** | 6.94 | 6.94 | 4.31 | 4.37 |
| **SS** | 7.61 | 7.58 | 6.87 | 6.66 |
| **EW 0** | 5.33 | 5.40 | 3.27 | 3.43 |
| **EW 7** | 5.15 | 5.25 | 3.30 | 3.46 |
| **EW 28** | 5.20 | 5.18 | 3.30 | 3.46 |
| **EW 56** | 5.13 | 5.25 | 3.30 | 3.46 |
| **EW 140** | 5.16 | 5.16 | 3.29 | 3.45 |
| **EW** | 6.88 | 6.92 | 3.83 | 3.85 |
| **L.s.d. (0.05)** | 0.43 | | 0.42 | |
| **p-value** | 0.663 | | 0.804 | |

*SS smelter slag

*EW electrowining waste

*Ia Inanda soil (A horizon)

*SS 0, 7, 28, 56, 140 Ia soil treated with SS and sampled after 0, 7, 28, 56, and 140, respectively

*EW, 7, 28, 56, 140 Ia soil treated with EW and sampled after 0, 7, 28, 56, and 140, respectively

**Appendix 8. 1** A comparison between sequential (SEP) and batch (BEP) extraction final pH for the reducible (RF) and oxidisable (OF) fractions

| Material | RF | | OF | |
|---|---|---|---|---|
| | **BEP** | **SEP** | **BEP** | **SEP** |
| **Ia** | 2.47 | 2.32 | 2.41 | 2.29 |
| **SS 0** | 5.22 | 3.43 | 3.12 | 2.46 |
| **SS 7** | 4.58 | 4.28 | 2.82 | 2.79 |
| **SS 28** | 4.92 | 3.35 | 3.07 | 2.42 |
| **SS 56** | 5.25 | 3.36 | 3.14 | 2.45 |
| **SS 140** | 5.11 | 3.56 | 3.06 | 2.47 |
| **SS** | 6.30 | 5.86 | 4.02 | 3.65 |
| **EW 0** | 2.81 | 2.25 | 2.38 | 2.35 |
| **EW 7** | 2.85 | 2.25 | 2.38 | 2.35 |
| **EW 28** | 2.82 | 2.22 | 2.37 | 2.35 |
| **EW 56** | 2.85 | 2.25 | 2.39 | 2.35 |
| **EW 140** | 2.82 | 2.24 | 2.38 | 2.35 |
| **EW** | 5.37 | 4.75 | 2.88 | 2.65 |
| **L.s.d. (0.05)** | 0.56 | | 0.190 | |
| **p-value** | 0.003 | | 0.008 | |

*SS smelter slag

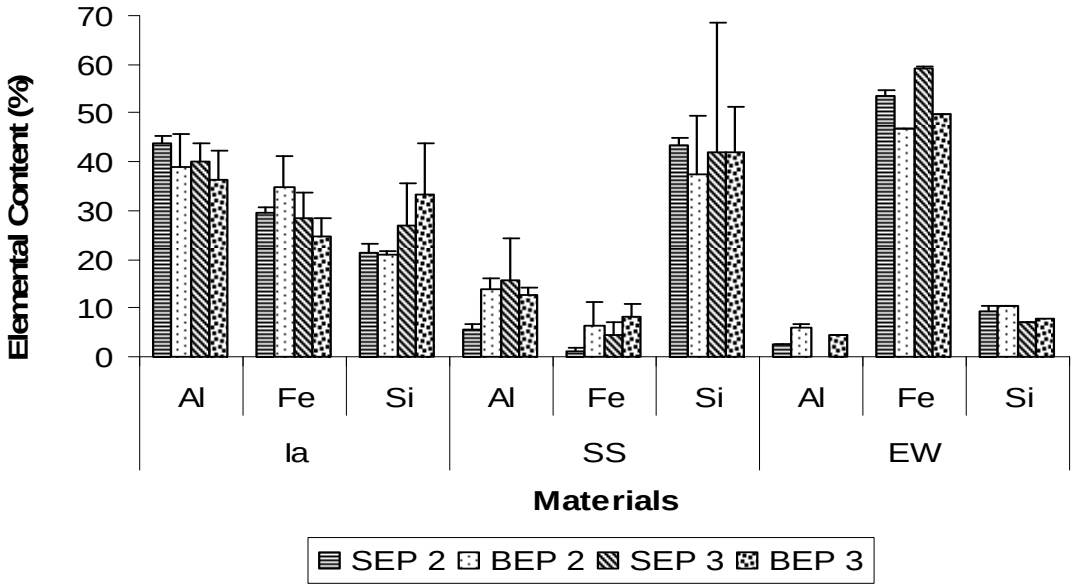
*EW electrowining waste

*Ia Inanda soil (A horizon)

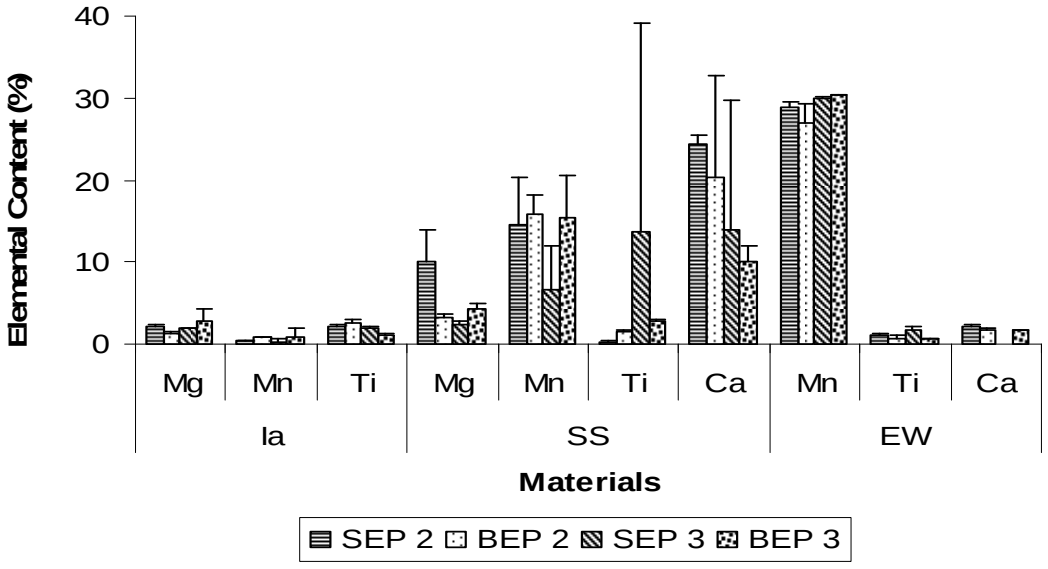
*SS 0, 7, 28, 56, 140 Ia soil treated with SS and sampled after 0, 7, 28, 56, and 140, respectively

*EW, 7, 28, 56, 140 Ia soil treated with EW and sampled after 0, 7, 28, 56, and 140, respectively

**Appendix 8. 2** A comparison between sequential (SEP) and batch (BEP) extraction residue (a) Al, Fe, and Si (b) Mg, Mn, Ca, and Ti composition for Inanda soil (Ia), smelter slag (SS), and electrowining waste (EW) after hydroxylammonium chloride (SEP 2 and BEP 2) and hydrogen peroxide (SEP 3 and BEP 3) extraction

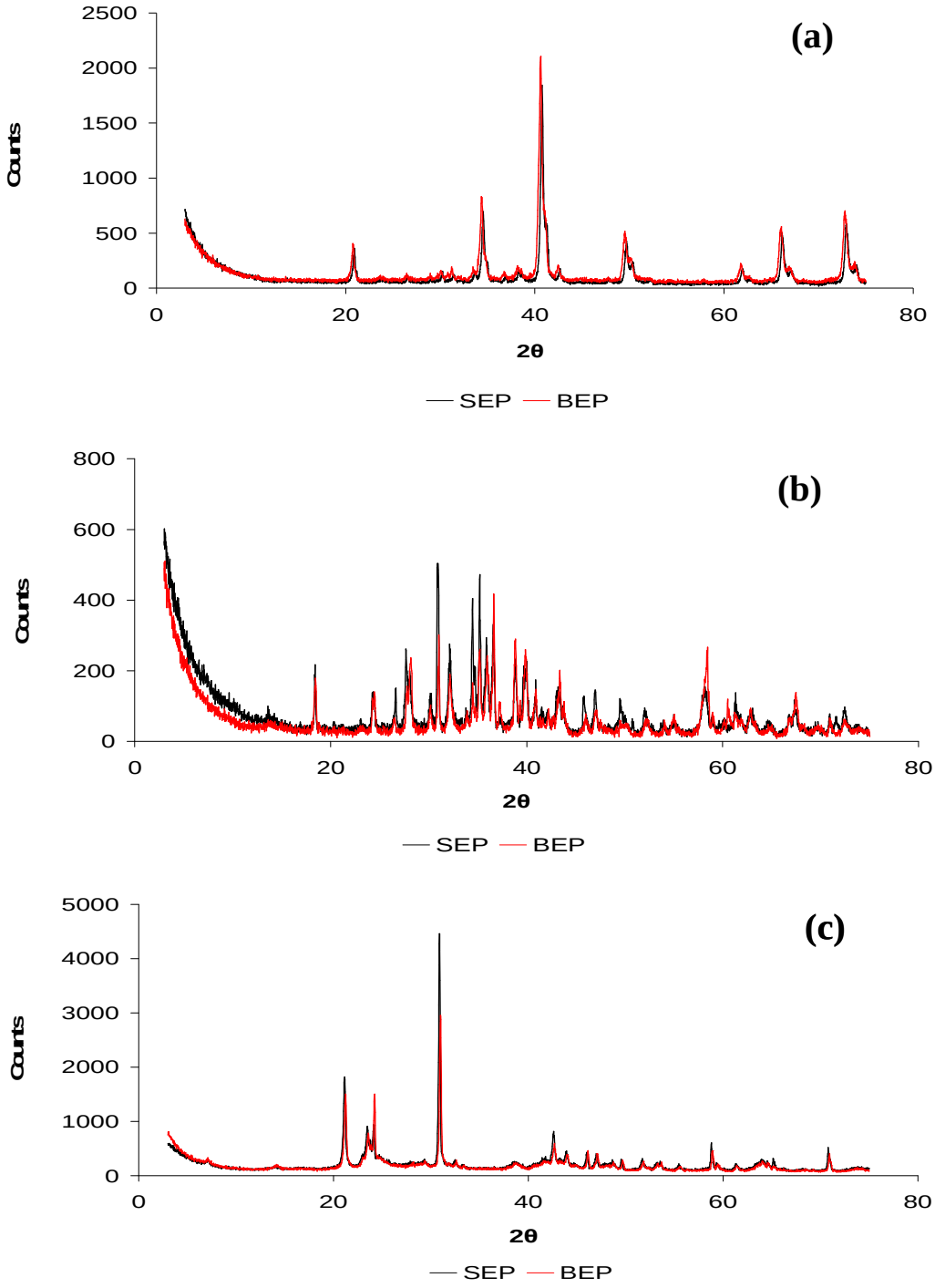



(a)




(b)

**Appendix 8. 3** The X-ray diffraction patterns for the random orientated powder samples of (a) the electro-winning waste, (b) smelter slag, and (c) A horizon of Inanda soil form residues left after sequential (SEP, black line) and batch hydroxylammonium chloride (BEP, red line) extractions



**Appendix 8. 4** The X-ray diffraction patterns for the random orientated powder samples of (a) the electro-winning waste, (b) smelter slag, and (c) A horizon of Inanda soil form residues left after sequential (SEP, black line) and batch hydrogen peroxide (BEP, red line) extractions